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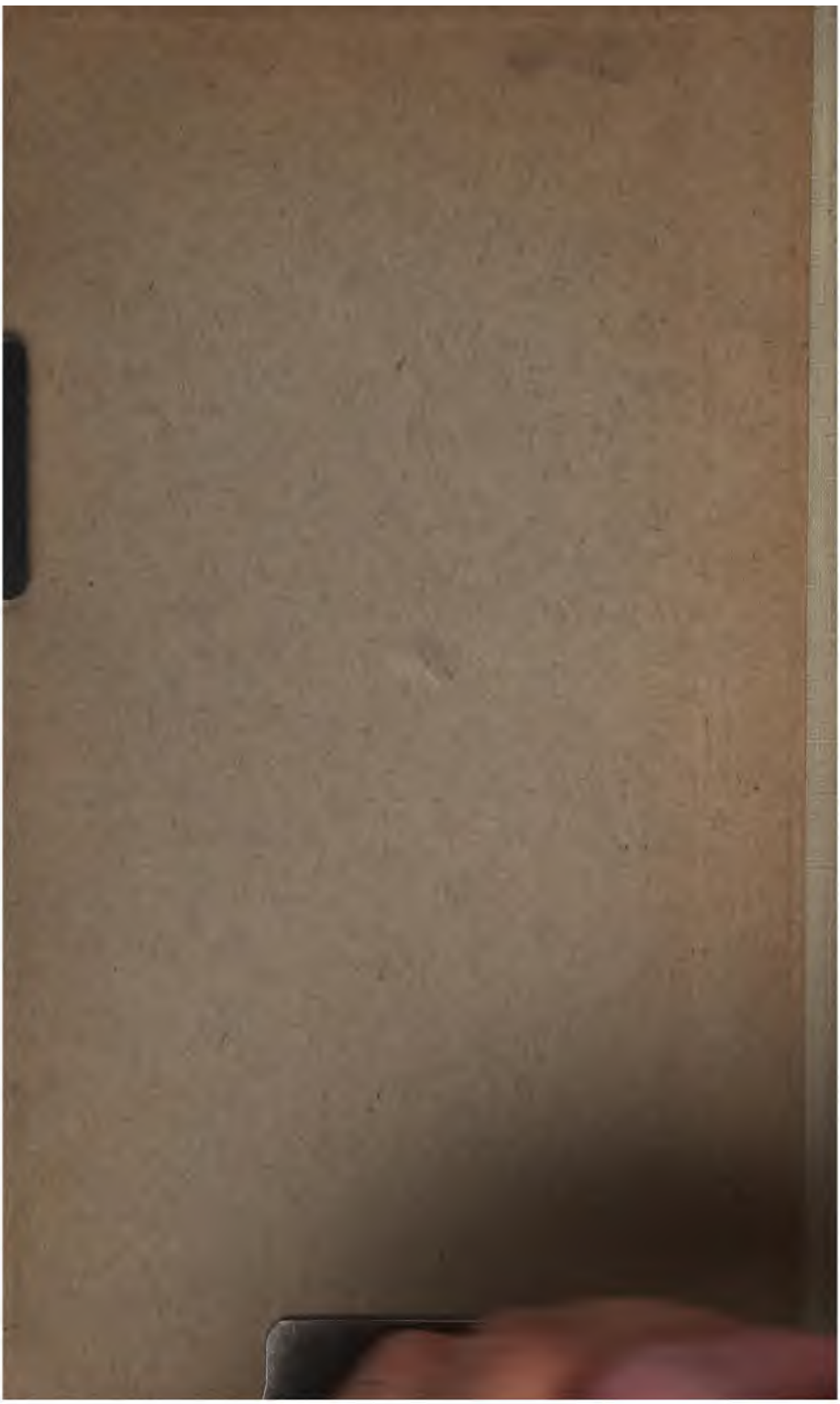

QUALITATIVE CHEMICAL ANALYSIS

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QUALITATIVE CHEMICAL ANALYSIS

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Qualitative Chemical Analysis

FROM THE STANDPOINT OF

Solubilities, Ionization and Mass Action

BY

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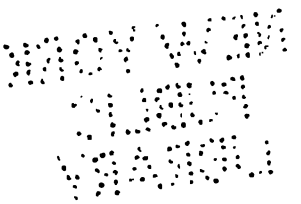

Preface

This work is intended to be both educational and practical. The subject is developed in such a way as to make the student familiar with the properties and reactions of all the substances with which he deals and also to so teach him the underlying principles that he will have an intelligent understanding of all the processes. At the same time the system is such as to give the analyst a rapid and accurate practical method of qualitative analysis.

Solubilities, the theory of electrolytic dissociation and the law of mass action have received an unusual amount of attention and have been freely used whenever they seemed to afford the best explanation of the reactions and phenomena under consideration. At the same time their application has not been forced when other principles were more satisfactory.

The classification of the kations is practically that which is usually found in the text-books. The grouping of the anions is essentially that given in Boettger's Qualitative Analysis, but the systematic method for their separation and identification is a new arrangement.

I have freely consulted and drawn from the chemical journals and all the books within my reach and desire here to express my obligation to these various sources too numerous to be mentioned. On another page I have given a list of the works to which I am most indebted and which I heartily recommend to the reader.

Properties and reactions are given with unusual fullness and the student is expected to become practically so familiar with them that he will be able not only to discover what ions are present in the unknown, but also to ascertain definitely what free elements or compounds compose the body under examination. The process of analysis is thus not one of simple routine, but constantly appeals to the student's knowledge of facts and principles, and the correctness of his conclusions depends upon close observation and good judgment.

Several methods new or uncommon have been introduced, generally as alternatives. Among these I may mention the cobaltinitrite test for potassium, the Benedict method for cobalt and nickel, the basic acetate method for aluminum and chromium and the alcohol method for calcium and strontium and the use of sodium carbonate for the separation of the divisions of Group 2.

In order to prevent confusion, the basic groups have been numbered and the acid groups lettered. Names have been given to the basic groups and it is recommended that students be taught to refer to them by name rather than number.

Mr. W. C. Moore has kindly read both the manuscript and the proof, and I am greatly indebted to him for valuable criticisms and suggestions.

Where so many details are involved it is probable that mistakes have been made and I ask the kindly indulgence of the reader. I shall be specially grateful to any one who will call my attention to errors of any sort.

Nashville, Tennessee. J. I. D. HINDS.
July, 1910.

Preface to the Second Edition

The call for a second edition of this work has given me opportunity to remove minor errors and to introduce some new matter, especially a convenient and expeditious method for precipitating the Copper-Arsenic Group and separating its Divisions, and the Sulfite Method for separating calcium and strontium. I hope these will prove of service to those who use the book.

Lebanon, Tennessee. J. I. D. HINDS.
June, 1912.

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QUALITATIVE ANALYSIS

PART I

PRINCIPLES AND METHODS OF QUALITATIVE ANALYSIS

Chapter I

INTRODUCTORY

Analytical Chemistry.—The subject of chemistry is divided into various branches according to the purpose for which it is treated. We thus have Theoretical Chemistry, Descriptive Chemistry, Physical Chemistry, Analytical Chemistry and so forth. In analytical chemistry the object is to investigate a single substance or a mixture so as to ascertain its composition. There are two main divisions of this branch.

In the first place, we may seek to know what compounds or elements are found in the given substance. If, for example, the substance is common salt, we shall find by the analysis that it contains the elements sodium and chlorin. This division is called **Qualitative Analysis.**

In the second place, we may desire to know in what proportion by weight or volume the elements or compounds enter into the given substance. In the above example we may learn not only that common salt contains sodium and chlorin, but also that these elements enter the compound in the proportion of 23 parts of sodium to 35.45 parts of chlorin by weight. Again, in the electrolysis of water we find that the gases collected in the separate tubes are in the proportion of two parts of hydrogen to one part of oxygen by volume. This divison of the subject is called **Quantitative Analysis.**

The subject of this work is Qualitative Analysis. In its treatment the investigations will be limited to the more common elements and inorganic compounds and the more important organic acids.

Elemental and Proximate Analysis.—If the problem is to ascertain what chemical elements enter the unknown, the process is called **Elemental Analysis**. If the inquiry regards the compounds or radicals which may be present, the procedure is called **Proximate Analysis**. Since the elemental composition of compounds is generally known, the object will be primarily to determine what compounds are present, and qualitative analysis will usually be proximate. Elemental analysis is in most cases not instructive. For example, we might find that a substance contained carbon, oxygen, hydrogen, sodium and chlorin without being able to infer that it was a mixture of sugar and common salt. It will, therefore, be the business of the analyst to learn, so far as possible, what compounds are present in the substance under examination.

Identification of Substances.—A substance is identified by its properties and its reactions. We recognize sulfur by the fact that it is yellow, light, insoluble in water, and that it burns with a stifling odor; gold by its yellow color, its metallic luster, its high specific gravity and its insolubility in acids; sodium chlorid by its salty taste, its solubility in water, its cubical crystals, and the white, curdy precipitate which it yields with silver nitrate. The sum total of properties fixes absolutely the identity of a substance. In most cases only a few of the properties and reactions need be observed in order to insure a safe conclusion.

While the identification of a single inorganic substance is not usually difficult, the number of such substances is so great that to identify them independently would be an almost endless task. When mixtures are involved, the problem is much more complicated. It happens, however, that most inorganic compounds have a sort of binary character, being separable into two parts, simple or complex, each of which gives characteristic reactions. These parts are the ions of ordinary solutions. This fact renders the

problem much more simple. For example, silver nitrate separates into the silver ion, Ag^+, and the nitrate ion, NO_3^-. The silver ion has the same properties in all soluble silver salts, and the nitrate ion exhibits the same reactions in all the nitrates. Hence a study of these two ions gives some knowledge concerning all silver salts and all nitrates. The more common compounds yield about thirty kations and as many anions. These would make nine hundred compounds, supposing that each kation combines with each anion. In order to identify the nine hundred compounds, it is only necessary to be able to identify the sixty ions.

Chapter II

METHOD OF ANALYSIS

General Method.—The general method of qualitative analysis will consist in first separating the unknown mechanically or chemically into its constituent parts (compounds, elements or ions) and then recognizing these parts by their properties and reactions. This will be illustrated by the following outline:

1. The unknown is a single substance. The procedure may follow one of three lines:

a. The substance may be identified directly by its properties and reactions. Examples of substances which may be thus identified are water, alcohol and common salt.

b. Changes may be brought about by which the unknown is converted into substances more easily identified. Mercuric oxid is decomposed by heat into mercury and oxygen, two elements easily recognized; limestone is decomposed by heat into calcium oxid and carbon dioxid; sulfur burns to sulfurous oxid recognized by its odor.

c. The substance may be ionized by solution and the ions identified by their properties and reactions. See *b* below.

2. The unknown is a mixture. In this case there are two lines of procedure:

a. The parts are separated mechanically or chemically and then identified as in 1 above.

b. The mixture is brought into solution thus setting free all the ions and these are removed successively as known compounds by precipitation and filtration.

The last process is of most general application and is the one used in systematic schemes of qualitative analysis.

Division of the Subject.—Since the substances in solution are ionized, the reactions will be between the ions and will indicate

their presence rather than that of the elements and compounds. Nearly all acids, bases and salts separate into two kinds of ions, one positive or basic, the kation, and the other negative or acidic, the anion. Qualitative analysis may, therefore, be very properly divided into two parts, **Basic Analysis** and **Acidic Analysis.** The kations are generally simple, representing positive elements or metals, in a few cases radicals such as ammonium. The anions may be simple, representing negative elements or non-metals, such as the halogens, oxygen and sulfur, but are generally more or less complex, as hydroxyl, cyanogen, or the negative radicals of acids and salts.

Method of Basic Analysis.—The general method of basic analysis is based upon (1) separation by precipitation and filtration and (2) final identification by characteristic properties and reactions. The logical method is that of division and exclusion. A reagent is added containing an ion which will form with some of the ions in the solution insoluble compounds. When these have been removed by filtration, another reagent is added which will precipitate other ions, and so on until all have been removed. The ions are therefore removed in groups. Each group precipitate is dissolved and further separated in a similar manner, until finally each ion is isolated and identified. The selection of the group reagent is entirely arbitrary and is based upon convenience. Usually five groups are determined by the five reagents, hydrochloric acid, hydrogen sulfid, ammonium hydroxid, ammonium sulfid, ammonium carbonate. A sixth group for which there is no reagent contains the ions not removed by the group reagents. The grouping used in this work is given on page 6.

Method of Acidic Analysis.—The anions or acid radicals do not admit of successive group and individual separations. They must be identified by special tests. Group reactions are used to indicate which anions may be present and which are certainly absent. Many of the anions will have been found in the course of the basic analysis and the problem really is generally very simple.

Analytic Groupings

Groups of Kations or Metals.—Various schemes of analysis have been proposed from time to time. The grouping followed in this work is that which has been found most generally practical.

Group 1: Metals whose chlorids are insoluble in dilute acids. Reagent, dilute hydrochloric acid.

Metals: Silver, mercurous mercury, lead.

Ions: Ag^{+}, Hg_2^{++}, Pb^{++}.

Group 2: Metals, other than those of Group 1, whose chlorids are soluble and whose sulfids are insoluble in dilute acids. Reagent hydrogen sulfid in the presence of dilute hydrochloric acid.

This group is divided into two sub-groups determined by solubility in ammonium sulfid.

Division A. Metals of Group 2 whose sulfids are insoluble in ammonium sulfid.

Metals: Mercuric mercury, lead, bismuth, copper, cadmium.

Ions: Hg^{++}, Pb^{++}, Bi^{+++}, Cu^{++}, Cd^{++}.

Division B. Metals of Group 2 whose sulfids are soluble in ammonium sulfid.

Metals: Arsenic, antimony, tin.

Ions: As^{+++}, As^{+++++}, Sb^{+++}, Sb^{+++++}, Sn^{++} Sn^{++++}.

Group 3: Metals, other than those of Groups 1 and 2, whose hydroxids are insoluble in ammonium hydroxid in the presence of ammonium chlorid and whose acetates are hydrolized by heat with formation of basic acetates. Reagent, ammonium hydroxid in slight excess in presence of ammonium chlorid.

Metals: Iron, chromium, aluminum.

Ions: Fe^{++}, Fe^{+++}, Cr^{+++}, Al^{+++}.

Group 4: Metals, other than those of Groups 1, 2 and 3, whose sulfids are insoluble in ammonium sulfid. Reagent, ammonium sulfid in presence of ammonium hydroxid and ammonium chlorid.

Metals: Zinc, manganese, cobalt, nickel.

Ions: Zn^{++}, Mn^{++}, Co^{++}, Ni^{++}.

Group 5: Metals, other than those of Groups 1, 2, 3 and 4, whose carbonates are insoluble in ammonium hydroxid in the presence of ammonium chlorid. Reagent, ammonium carbonate with ammonium hydroxid and ammonium chlorid.

Metals: Barium, strontium, calcium.

Ions: Ba^{++}, Sr^{++}, Ca^{++}.

Group 6: Ions which have been left in the solution from which the other groups have been removed and for which there is no group reagent.

Metals: Magnesium, sodium, potassium, lithium, hydrogen.

Radical. Ammonium.

Ions: Mg^{++}, Na^{+}, K^{+}, Li^{+}, H^{+}, NH_4^{+}.

Groups of Anions or Acid Radicals.—There is much difference of opinion among analysts as to the best grouping of the anions and hardly two books are in exact agreement. The grouping followed in this work is given in detail in Chapter XIII. It is tabulated below for convenience of reference. Letters are used to prevent confusion with basic groups.

BASIC GROUPS

Group 1	Group 2A	Group 2B	Group 3
Silver	Mercuric mercury	Arsenic	Iron
Mercurous mercury	Lead	Antimony	Chromium
Lead	Bismuth	Tin	Aluminum
	Copper		
	Cadmium		

Group 4	Group 5	Group 6
Zinc	Barium	Magnesium
Manganese	Strontium	Sodium
Cobalt	Calcium	Potassium
Nickel		Lithium
		Hydrogen
		Ammonium

ACIDIC GROUPS

Group A	Group B	Group C
Sulfate	Fluorid	Phosphate
Fluosilicate	Chromate	Arsenite
	Dichromate	Arsenate
	Sulfite	Borate
	Thiosulfate	Silicate
	Oxalate	Carbonate
		Tartrate
		Citrate

Group D1	Group D2	Group E
Bromid	Chlorid	Nitrate
Iodid	Cyanid	Cyanate
Sulfid	Thiocyanate	Chlorate
Ferrocyanid	Iodate	Perchlorate
	Bromate	Formate
	Ferricyanid	Acetate
	Permanganate	
	Nitrite	

THE RARE ELEMENTS

The rare elements are mostly basic and, if they are present, are precipitated along with the kations. For their treatment the student is referred to the larger works on Qualitative Analysis. They fall into the analytical groups as follows:

Group 1: Thallium, tungsten.

Group 2: Platinum, gold, palladium, rhodium, iridium, osmium, ruthenium, selenium, tellurium, molybdenum, germanium and gallium.

Group 3: Uranium, indium glucinum, zirconium, thorium, yttrium, cerium, lanthanum, columbium, tantalum, titanium, gallium, praseodymium, neodymium.

Group 4: Tungsten, vanadium.

Group 6: Lithium, rubidium, caesium.

Molybdenum, tungsten, vanadium, selenium, tellurium, and several others are rather acidic than basic.

Chapter III

SEPARATIONS

When mixtures are under examination, whether it be the original substance or mixtures obtained by chemical action, it will generally be necessary to separate the constituents before they can be identified. The separation may be purely mechanical, or it may be associated with physical or chemical action. The mechanical and physical operations are here described, while those that involve chemical change are discussed under the head of reactions.

Decantation.—When a liquid containing a solid in suspension, together with substances in solution, is allowed to stand, the solid settles to the bottom of the vessel and the clear liquid may be poured away. The solid is washed by adding water, or the solvent whatever it may be, and repeating the settling and decantation as often as may be necessary.

Filtration.—The more common method of separating a suspended solid from a liquid is by filtration. A specially prepared filter paper is placed in a funnel and the mixture is transferred to it. The liquid runs through while the solid remains on the paper.

Filtration is made more rapid by the use of the filter pump. A perforated platinum cone, or a cone of hardened paper, is placed in the funnel, the filter is neatly folded, moistened and pressed closely against the glass, and the funnel is inserted in the flask attached to the filter pump. The suction draws the liquid through rapidly and the cone prevents the breaking of the filter under the pressure.

Filtration is also facilitated by heat, hot liquids passing through more rapidly than cold ones.

Washing.—The solid which has been separated by filtration must be washed to remove the adherent liquid which may contain substances in solution. If the method of settling and de-

cantation has been used, but little washing will be necessary. After the solid has been transferred to the filter a stream of water, or of the washing fluid, is poured around the margin of the filter so that the filter as well as its contents may be washed. This process is continued until a drop of the liquid from the point of the funnel does not react for the substances supposed to be in the solution. The washing fluid is thrown upon the filter from the washing bottle, or is conducted to the desired point with the stirring rod.

Evaporation.—Solids are recovered from solution by evaporation. If the free flame is used, overheating should be avoided, especially near the end of the process. It is generally best to use the steam-bath.

Crystallization.—When solutions are evaporated the dissolved solids separate, usually in the form of crystals. The less soluble substances separate first and may be removed. By redissolving the removed crystals and evaporating several times the pure substance may be obtained. The process is called **fractional crystallization.**

Distillation.—By distillation a liquid may be separated from all the non-volatile solids which it may contain in solution. Liquids may often be separated from one another by fractional distillation.

Chapter IV

SOLUTIONS

Solution.—The first step in the course of the usual analysis after the preliminary examination is to secure the ionization of all the substances present. This is accomplished by bringing them into solution. Water is the common and most universal solvent and the most powerful ionizing agent. Its solvent action is greatly assisted by the presence of other substances, especially acids, alkalis and salts. The substance in solution, called the **solute,** is generally the thing under investigation and may be almost any chemical element or compound.

Solutions possess many striking characteristics, of which only those will be treated in this work which are of special importance in qualitative analysis. For the full discussion of the subject the student is referred to works on Physical Chemistry.

Solubility.—Substances vary greatly in solubility. Water dissolves three times its weight of calcium permanganate and one-half its weight of sodium sulfate, while it takes only one part of barium sulfate in 400,000 and of silver iodid one part in 350,000,000.

Solubility is measured in various ways, usually as the number of grams contained in a liter of the solution. If the substance is very soluble, the volume of the solution will be greater than that of the water and then the number of grams contained in a given weight of the solution may be taken as the solubility. For some purposes it is more convenient to use the number of molecular weights or moles which are contained in a liter of the solution. This is called **concentration.**

Concentration.—It has been found that the properties of solutions vary, not with the weight of the solute in a given volume, but with multiples of the formula weight. It is convenient, therefore, to measure concentration by formula weights. The **mol** or **mole** is the gram molecular weight, the **gram ionic weight** is the weight in grams equal to formula weight of the ion, the

gram equivalent is the number of grams equal to the equivalent weight. The **equivalent weight** is that which corresponds to one atom of hydrogen in the acid or base or that which has replaced it in the salt. For example, the equivalent weight of HCl, HNO_3, $KClO_3$, KHO, and so forth, is identical with the molecular weight; that of H_2SO_4, H_2CrO_4, $BaCl_2$, CaH_2O_2, is one-half the molecular weight; that of H_3PO_4, AlH_3O_3, $AlCl_3$, is one-third of the molecular weight. A **normal solution** is one which contains one gram equivalent to the liter. Solutions may be decinormal, centinormal, five normal, and these concentrations are indicated thus, 0.1 N, 0.01N, 5N. To make normal solutions a liter should contain of the following substances the quantities indicated: NaCl 58.45 grams, H_2SO_4 49 grams, $AlCl_3$ 44.4 grams.

Concentration is often, for convenience, expressed as percentage, or as parts in one thousand or in a million.

Osmotic Pressure.—If an aqueous solution be conveyed by a tube to the bottom of a vessel containing pure water, so that the water overlies the solution, it will be found after the lapse of some time that the solution and solvent have mixed. If a partition be interposed which is permeable to the solvent but not to the solute, an upward pressure will be exerted. This is called **osmotic pressure.** Its cause is not known, but it may be provisionally regarded as the pressure required to prevent the dilution of a solution in contact with the solvent. Let the student read this subject in some work on Physical Chemistry.

The following facts in regard to osmotic pressure have been proven by careful investigation:

1. Osmotic pressure is proportional to the concentration.

2. Osmotic pressure is proportional to the absolute temperature.

3. Osmotic pressure is equal to the pressure which the solute would exert as a gas occupying the same volume as the solution.

4. The osmotic pressure of a normal solution is 22.4 atmospheres; that of a solution which contains a mole in 22.4 liters is one atmosphere, the temperature being 0°.

5. Equal volumes of different solutions having equal osmotic pressures contain the same number of molecules.

6. Dissociated substances give a higher osmotic pressure, each ion exerting the same pressure as the undissociated molecule.

Electrolytes.—If the electrodes of a battery are placed in pure water no perceptible current passes. If a soluble acid, base or salt is added to the water the solution becomes at once a conductor and at the same time the solute undergoes decomposition. Such substances are called **electrolytes** (things decomposed by electricity).

Ions.—In the year 1833 Faraday explained the above action by supposing that the molecules of the solute were divided into two parts, the one carrying positive and the other negative electricity. These parts he called **ions** (goers). Those positively charged he called **kations** (down goers) because they travel with the current toward the kathode, those negatively charged he called **anions** (up goers) because they go in the opposite direction toward the anode. As long as the two kinds of ions exist together in the solution there is equilibrium, but when an electrically charged body is introduced, the equilibrium is disturbed. The electrodes of a battery, for example, will attract the ions of opposite sign, causing them to migrate or move, the kations toward the kathode and the anions toward the anode. On arriving at the electrodes the ions are relieved of their electric charges and are set free as molecular substances. Such separation is called **electrolysis** (decomposition by electricity).

Electroneutrality.—Solutions containing ions are usually electrically neutral and contain equal quantities of positive and negative ionic charges. Ions will, therefore, appear and disappear in pairs positive and negative. Thus in the oxidation of ferrous ion by means of chlorin the formation of each chlorid ion compels a ferrous ion to take an additional positive charge:

$$Fe^{++} + Cl = Fe^{+++} + Cl^{-}.$$

Electroaffinity.—Some ions hold the electric charge more strongly than others, or have a greater electroaffinity, that is

are relatively more positive or negative. **Strong ions** as a rule form easily soluble compounds which are highly dissociated in solution, **weak ions** form sparingly soluble compounds which dissociate but slightly. Kations of high electroaffinity are found in the strong alkalis, and strong anions form the strong acids; while weak kations and anions are found in the corresponding weak bases and acids.

When a substance which will form strong ions comes in contact with weak ions, the latter lose their ionic charges and become neutral molecules, while the former passes into the ionic state. It is in this way that hydrogen is liberated from acids by metals, and that metals displace from their compounds metals of the lower electroaffinity. If a strip of zinc is placed in a solution of lead, the lead is set free while the zinc goes into the solution as zinc ion:

$$Zn + Pb^{++} = Zn^{++} + Pb.$$

So also lead displaces copper and copper displaces mercury. These four elements stand, therefore, in the order of decreasing electroaffinity zinc, lead, copper, mercury. Chlorin displaces bromin, bromin iodin and iodin sulfur. The electroaffinity series for these four elements is chlorin, bromin, iodin, sulfur.

The principal ions are arranged below according to decreasing electroaffinity. Each one in the neutral state should be able to take the electric charge from any one that follows it.

Kations: K^+, Na^+, Li^+, Ba^{++}, Sr^{++}, Ca^{++}, Mg^{++}, Al^{+++}, Mn^{++}, Zn^{++}, Cd^{++}, Fe^{++}, Co^{++}, Ni^{++}, Pb^{++}, H^+, Bi^{+++}, As^{+++}, Sb^{+++}, Sn^{++}, Cu^{++}, Ag^+, Hg^{++}, Pt^{++++}, Au^{+++}.

Anions: F^-, NO_3^-, ClO_3^-, Cl^-, SO_4^{--}, Br^-, I^-, PO_4^{---}, CO_3^{--}, CrO_4^{--}, SiO_3^{--}, HS^-, $H_2BO_3^-$, HO^-, CN^-, O^{--}, S^{--}.

Dissociation.—By dissociation is meant a reversible reaction which results in the decomposition of molecules (1) into simpler molecules, (2) into atoms or radicals, (3) into ions.

The first case includes many reversible reactions whose di-

rection depends upon conditions such as temperature and pressure. The decomposition of calcium carbonate by heat and the formation of carbonic acid by pressure are examples:

$$CaCO_3 \rightleftharpoons CaO + CO_2, \qquad H_2CO_3 \rightleftharpoons H_2O + CO_2.$$

The second case is like the first except that the parts are not saturated molecules. Examples are the decomposition of hydrochloric acid at high temperatures into hydrogen and chlorin, and the formation under conditions of cold and pressure of chlorin tetroxid from chlorin dioxid:

$$HCl \rightleftharpoons H + Cl, \qquad Cl_2O_4 \rightleftharpoons 2ClO_2.$$

The third case is ionization, which will be more fully discussed.

Electrolytic Dissociation or Ionization.—The separation of compounds into ions is called **ionization** or **electrolytic dissociation.** Solids, liquids and gases scarcely ionize, but under the influence of certain agents such as electricity, heat and radioactivity they undergo a limited dissociation. In aqueous solution most substances are more or less ionized. Exceptions are found in many organic compounds like sugar. Acids, bases and salts, three classes which include most inorganic substances, all ionize more or less when dissolved in water.

When a molecule undergoes electrolytic dissociation, an equal number of positive and negative electric charges appear upon the ions, so that the solution remains electrically neutral:

$$NaCl \rightleftharpoons Na^+ + Cl^-, \qquad BaCl_2 \rightleftharpoons Ba^{++} + 2Cl^-.$$

The unit charge is constant being 96,530 coulombs of electricity for each gram equivalent of a univalent ion. In terms of recent theory, the kation has lost and the anion gained an **electron.** The electron is the ultimate particle or atom of negative electricity whose mass is about one thousandth that of the hydrogen atom.

Methods of Ionization.—Wilhelm Ostwald of Leipzig has shown that ionization may take place in four different ways:

1. By dissociation through an ionizing agent, as when acids,

bases and salts are dissolved in water, or when gases are subjected to electric or radioactive influence:

$HNO_3 \rightleftharpoons H^+ + NO_3^-$, $H_2SO_4 \rightleftharpoons H^+ + H^+ + SO_4^{--}$.

Ionization through the action of water is the most common method.

2. By chemical action in the presence of an ionizing agent, as when chlorin water acts on certain metals:

$$Au + 3Cl \rightleftharpoons Au^{+++} + Cl^- + Cl^- + Cl^-.$$

3. By transfer of electric charge, as when zinc displaces copper or when chlorin displaces iodin:

$Cu^{++} + Zn \rightleftharpoons Cu + Zn^{++}$, $I^- + Cl \rightleftharpoons I + Cl^-$.

4. By increase or diminution of electric charge, that is by change of valence, as in oxidation of compounds of metals:

$$Fe^{++} + Cl \rightleftharpoons Fe^{+++} + Cl^-.$$

This action is reversible, representing oxidation as the equation stands and reduction when it is reversed.

Ions of Acids, Bases and Salts.—Hydrogen ions are characteristic of the acids. They separate as positive ions while the remainder of the molecule constitutes the negative ion. The anion is a negative element or a negative radical. The following are examples:

$HCl \rightleftharpoons H^+ + Cl^-$ $HNO_3 \rightleftharpoons H^+ + NO_3^-$
$HCN \rightleftharpoons H^+ + CN^-$ $H_3AsS_4 \rightleftharpoons 3H^+ + AsS_4^{---}$.

If the acid is polybasic, the ionization may take place by steps:

$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$ $H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$
$HSO_4^- \rightleftharpoons H^+ + SO_4^{--}$ $H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{--}$
$HPO_4^{--} \rightleftharpoons H^+ + PO_4^{---}$.

Thus a solution of phosphoric acid may contain, besides the undissociated acid, the ions H^+, $H_2PO_4^-$, HPO_4^{--} and PO_4^{---}.

The first hydrogen atom goes off more readily than the others and thus weak polybasic acids may act like monobasic acids. The

ionization of the second H does not usually begin until the substance is about 50 per cent. dissociated as to the first H.

The characteristic ion of a base is the hydroxid ion, HO^-. When a base dissociates HO^- separates as the negative ion and the remainder of the molecule forms the positive ion. The kation is usually a metal, sometimes a positive radical. It may include a portion of the hydroxyl since the base may dissociate by steps as does the acid.

The following are examples:

$$KHO \rightleftharpoons K^+ + HO^- \qquad Ba(HO)_2 \rightleftharpoons BaHO^+ + HO^-$$
$$NH_4HO \rightleftharpoons NH_4^+ + HO^- \qquad BaHO^+ \rightleftharpoons Ba^{++} + HO^-.$$

A salt yields the positive ion of a base and the negative ion of an acid. The dissociation may be partial as in the case of acids and bases. The following are examples:

$$KCl \rightleftharpoons K^+ + Cl^- \qquad K_2SO_4 \rightleftharpoons K^+ + KSO_4^-$$
$$CaSO_4 \rightleftharpoons Ca^{++} + SO_4^{--} \qquad KSO_4^- \rightleftharpoons K^+ + SO_4^{--}.$$

Acid salts owe their acidity to the hydrogen which they contain,

$$KHSO_4 \rightleftharpoons H^+ + K^+ + SO_4^{--}.$$

Naming the Ions.—There has not so far been a general agreement as to the naming of ions. A very simple method has been adopted in this book. The name is taken from the name of the compound from which the ions are supposed to be derived. Kations take the usual terminations ic and ous with the prefixes per and hypo, while the anions end in id, ite, and ate, also with the prefixes per and hypo. The following examples will illustrate:

KI yields potassium ion K^+ and iodid ion I^-.

$FeCl_3$ yields ferric ion Fe^{+++} and chlorid ion Cl^-.

$FeSO_4$ yields ferrous ion Fe^{++} and sulfate ion SO_4^{--}.

NaCNS yields sodium ion Na^+ and thiocyanate ion CNS^-.

$BaSiF_6$ yields barium ion Ba^{++} and fluosilicate ion SiF_6^{--}.

Extent of Dissociation.—The extent to which a particular substance ionizes in aqueous solution depends primarily upon the

nature of the substance itself, varying from almost complete dissociation in decinormal hydrochloric acid to one mole in more than ten million liters of pure water. The degree of dissociation is influenced slightly by changes of pressure and temperature and profoundly by changes of concentration.

Concentration and Ionization.—Ionization increases with dilution and there is a certain concentration for each substance at which dissociation is complete. This is somewhat improperly called **infinite dilution.** In the following table is given for illustration the per cent. of dissociation of potassium chlorid and of acetic acid for various concentrations at 18°. The concentrations are in moles to the liter.

Concentration	1	0.1	0.01	0.001	0.0001	0.00004 moles
Potassium chlorid...	74.85	85.30	93.37	97.26	98.71	100.00% dis.
Acetic acid	0.37	1.30	4.05	11.62	27.57	50.00% dis.

Complete Dissociation.—If the solution is made sufficiently dilute the dissociation will be complete, that is, no undissociated molecules will remain. This is practical, however, only in the case of strong electrolytes. Even with these the volume of water is quite large. For complete ionization at the ordinary temperature a gram equivalent of hydrogen chlorid must be dissolved in 500 liters of water, while sulfuric acid requires 8,000, and acetic acid about 30 millions. The strong electrolytes are rather highly dissociated in normal and decinormal solutions.

Dissociation and Chemical Activity.—Chemical activity in solutions is mainly dependent upon ions and those substances are as a rule most active which dissociate most highly. In equal concentrations, nitric acid is about twice as highly dissociated as sulfuric acid and may in a sense, be said to be twice as strong. Acetic acid of the same concentration is ionized less than one hundredth as much; it is therefore called a weak acid. Decinormal sodium hydroxid is sixty times as highly dissociated as

ammonium hydroxid of the same concentration. We call the former a strong base or alkali and the latter a weak one.

Electric Conductivity.—We have already seen that a solution containing an electrolyte is a conductor of electricity and that as the current passes the electrolyte is decomposed. It has been shown by careful investigations (1) that the ions are the conductors of the electricity; (2) that the conductivity depends upon the number of ions present, that is, upon the ionic concentration, and also upon the ionic migration velocities; (3) that the quantity of the electrolyte decomposed is approximately proportional to the conductivity, or to the quantity of electricity which passes. Conductivity, therefore, measures the degree of ionization, and is itself measured by the amount of decomposition. Like ionization it varies with pressure, temperature and concentration.

The investigation of the Russian Fanjung showed that with most electrolytes conductivity increases with great increase of pressure, the change reaching under a pressure of 250 atmospheres as much as 9 per cent. It has been observed that the formation of ions is often accompanied by a diminution of volume. If the volume be diminished by pressure, it naturally follows that more ions will be formed. The amount of the change through ordinary ranges of pressure is so small that it is usually ignored.

The effect of heat upon conductivity is greater than that of pressure and must be reckoned with. In most cases conductivity, which in a way measures ionization, increases with rising temperature. The increase in dilute solutions is various, averaging for salts about 2.5 per cent., for bases about 2 per cent., and for acids about 1.5 per cent. for each degree of change of temperature.

Conductivity is measured in reciprocal ohms by comparison with a standard resistance. The unit used is the conductivity of a column of a solution one centimeter long and one square centimeter in cross section which has a resistance of one ohm. Solutions of the stronger acids at their best conducting concentration have about this conductivity at 40°. The measurement

made in this unit is called **specific conductivity.** It is usually represented by the Greek letter kappa κ.

Conductivity depends largely upon concentration and for purposes of comparison it is more convenient to use what is called **equivalent** or **molecular conductivity.** This is the conductivity or **conductance,** as it is also called, of a solution which contains one equivalent or one mole of a solute between electrodes one centimeter apart and large enough to contain between them the whole of the solution. This value is usually represented by the Greek letter lambda λ, and may be found from the specific conductivity by multiplying κ by the number of cubic centimeters in which one equivalent is dissolved, or by dividing κ by the number of equivalents in each cubic centimeter of the solution.

If c is the concentration in equivalents per cubic centimeters and v the number of cubic centimeters which contains one equivalent, we shall have for the equivalent conductance

$$\lambda = \kappa v, \text{ or } \lambda = \frac{\kappa}{c}.$$

If V is the volume in liters which contains one equivalent and C the concentration in equivalents to the liter, then

$$\lambda = 1000\kappa V, \text{ or } \lambda = \frac{1000\kappa}{C}.$$

Molecular conductance, like ionization increases with dilution until it reaches a maximum. The molecular conductivities of potassium chlorid and of acetic acid at 18° and in various degrees of dilution are as follows:

MOLECULAR CONDUCTIVITIES AT 18°.

Concentration....	1	0.1	0.01	0.001	0.0001	Inf.
for KCl.....	98.2	111.9	122.5	127.6	129.5	131.2
for $C_2H_4O_2$	1.32	4.6	14.3	41.0	107.0	353.0

Conductivity and Ionization.—Since the ions are the conveyors of the electricity, the relation of the conductance to the degree of ionization may be expressed by the equation

$$a = \frac{\lambda_m}{\lambda_o},$$

in which a is the degree of dissociation, λ_m the molecular or equivalent conductance at any dilution, and λ_o the conductance at infinite dilution. This formula enables us to compute the degree of ionization when the conductance has been determined. Thus the percentages given under Concentration and Ionization on page 18 are computed from the conductivities given in the last paragraph above. The law does not rigidly apply in the case of strong electrolytes.

Illustrations.—*a.* The equivalent conductance of a decinormal solution of potassium chlorid at 18° is 112 reciprocal ohms, while at infinite dilution it is 130. The dissociation is therefore according to the rule $\frac{112}{130} = 0.8615$, or the substance is 86.15 per cent. ionized.

b. The equivalent conductance of decinormal acetic acid at 18° is 4.6 and the maximum conductance is 353. The dissociation is therefore $\frac{4.6}{353} = 0.013$, or 1.3 per cent.

Ionic Conductivity.—In an electrolytic cell the anions travel toward the anode and the kations toward the kathode, but generally not with equal velocities. In this way one ion may transfer more of the electricity than the other. Kohlrausch found that the number representing the molecular conductivity was composed of two parts, one of which refers to the anion and the other to the kation. The maximum molecular conductance of potassium chlorid, for example, is 130. Of this the anion carries 65.38 and the kation 64.62. The conductance of the ions being known, that of any of their compounds is obtained by addition. This principle is of great use, for it enables us to find the maximum conductance of many compounds for which experimental determination is impracticable. The dilution of acetic acid, for example, necessary to complete dissociation is so great, something like 100,000 liters to the mole, that its maximum molecular conductance cannot be determined. We can, however, find the conductance of hydrogen ion from strong acids and that of acetate ion from acetates. The former is 318 and the latter 35.

The sum of these numbers 353 is the maximum molecular conductance of acetic acid. A table in Part 5 contains the ionic mobilities or maximum equivalent conductivities of some of the more important ions at 18°, together with the temperature coefficient for each degree of rise.

Reaction Velocity.—Some chemical reactions like rusting of iron, solution of rocks through atmospheric agencies and decay of organic substances are very slow; others like combustion of coal, solution of metals in acids and the decomposition of potassium chlorate by heat proceed rapidly; still others like the explosion of dynamite, the ionization of solutes and the formation of precipitates are almost instantaneous. The speed of the reaction depends primarily upon that mysterious force known as chemical affinity, but there are various conditions which powerfully influence it. Those which are of the most importance to the analytical chemist are (1) change of temperature, (2) the presence of a catalyzer, (3) the degree of ionization, (4) the concentration or mass of the reacting substances.

1. As the temperature rises the velocity of a reaction generally increases in some sort of geometric proportion. "The inversion of cane-sugar proceeds five times as fast at 55° as at 25°; the conversion of ammonium cyanate into urea is fifty times as rapid at 57° as it is at 33°; the transformation of dibromsuccinic acid into bromomaleic acid goes three thousand times as rapidly at 101° as at 15°; and although the reaction between hydrogen and oxygen is so slow at 155° that no sign of combination can be detected for many months, yet, at about 600° the combination takes place with explosive violence." (Mellor's Chemical Statics and Dynamics, page 384.) The velocity of many reactions is greatly accelerated by the heat of the reaction itself. This is markedly the case when the reaction is highly exothermic.

2. Many reactions are greatly favored by the presence of a catalytic agent. Just how the catalyzer acts is not known, but its help is very useful in many analytic operations. Of all the substances which exert the catalytic action none are of more importance to the analyst than water and its ions. The presence

of moisture seems to be a necessary condition to the beginning of most chemical actions and water is the greatest of all ionizing agents.

3. In solutions reactions take place rapidly because the solutes are ionized. When the reacting substances are highly dissociated, precipitation is practically instantaneous, and even when the ionization is slight, the precipitate usually falls rapidly. Crystalline substances sometimes form slowly.

4. The speed of a chemical action depends also upon the concentration or mass of the acting substances. This condition is far reaching and is illustrated in the applications of the law of mass action, which will be discussed later.

The velocity of a reaction will generally change as the reaction proceeds, because the above conditions will change. An exothermic reaction will be accelerated by the heat produced. As a precipitate forms the number of ions and the active mass both diminish and also the speed of the reaction. Thus the velocity of a reaction will generally increase for a time and then gradually decrease until it approaches zero when the reaction is complete or when equilibrium is established.

Illustrations.—*a.* To illustrate the effect of heat on a reaction cover a piece of tin with hydrochloric acid and when the action is well under way apply heat.

b. To observe the effect of the heat of the reaction itself add a bit of zinc to some strong nitric acid. The action begins slow and increases rapidly as the liquid becomes hot.

c. To illustrate the effect of a catalytic agent add to a tube containing a strip of rather pure zinc 5 N sulfuric acid. When the action is under way, add a few drops of a solution of copper sulfate and note the increase of velocity.

d. To illustrate the effect of concentration drop bits of zinc into three test-tubes containing 4, 8 and 12 cubic centimeters of water respectively, then add to each one cubic centimeter of hydrochloric acid. Compare the reaction velocities by observing the rapidity with which the hydrogen is evolved.

e. To observe the influence of the degree of ionization drop

bits of calcium carbonate in three test-tubes and add to them respectively normal acetic, sulfuric and nitric acids. The first will scarcely act, the second will act slowly, the third rapidly.

In the following discussion temperature and pressure are supposed to remain unchanged and the influence of catalysis and ionization are ignored or included in the affinity coefficient. In the general reversible reaction

$$\underset{a}{A} + \underset{b}{B} \rightleftharpoons \underset{c}{C} + \underset{d}{D}$$

let k represent the force of affinity driving it to the right and k' that impelling it to the left, then the forward speed of the reaction, that is the number of moles of A and B which are changed in a unit of time, say in a minute, will be proportional to k, and in the same way the speed in the opposite direction will be proportional to k'. Now the speed will also be proportional to the number of moles present of the various substances which we may represent by the letters a, b, c and d. The forward velocity will then be $v = k\ a\ b$ and that in the opposite direction will be $v' = k'\ c\ d$. The actual velocity at any moment will be the difference between v and v', or $V = v - v' = k\ a\ b - k'\ c\ d$. When equilibrium is attained $v = v'$ and $k\ a\ b = k'\ c\ d$.

Illustration.—At 450° hydrogen iodid is about 0.2 dissociated into hydrogen and iodin and the equation and concentrations will be as follows:

$$\underset{c=0.8}{2HI} \rightleftharpoons \underset{a=0.1}{H_2} + \underset{b=0.1}{I_2}.$$

Since there are two molecules if H I the forward speed will be $k\ c^2$ while that in the opposite direction will be $k'\ a\ b$ and when there is equilibrium $kc^2 = k'ab$, or $\frac{k}{k'} = \frac{ab}{c^2} = \frac{0.1 \times 0.1}{(0.8)^2} = \frac{1}{64}$.

The velocity of union at this temperature is therefore 64 times as great as the velocity of dissociation.

Chemical Equilibrium.—Most reactions, possibly all, are reversible and under given conditions will continue in one direction until equilibrium is attained, that is until the speed of reaction in one direction is equal to that in the other. If, for

example, phosphorous chlorid and chlorin are mixed in molecular proportions, phosphoric chlorid will be formed according to the equation,

$$\underset{a}{PCl_3} + \underset{b}{Cl_2} \rightleftharpoons \underset{c}{PCl_5}.$$

The action will continue with diminishing velocity toward the right until the tendency to union is balanced by the tendency of the PCl_5 to dissociate, when it will stop with all three substances present.

The Law of Mass Action.—When a mixture of reacting substances has attained equilibrium, the reaction will be started again by increasing or diminishing the quantity present of any one of the substances. If, for example, hydrogen sulfid be added to a solution of cadmium chlorid, cadmium sulfid is precipitated, but not completely, because the hydrogen chlorid formed exerts a solvent action on the cadmium sulfid,

$$\underset{a}{CdCl_2} + \underset{b}{H_2S} \rightleftharpoons \underset{c}{CdS} + 2\underset{d}{HCl}.$$

If more H_2S is added, more CdS is precipitated; if hydrochloric acid is added, the precipitate dissolves. An excess of H_2S drives the reaction to the right while an excess of HCl turns it to the left.

If the letters *a, b, c* and *d* are used to represent the concentrations (number of gram equivalents to the liter within the sphere of the action) of the four substances, and *k* and *k'* the affinity factors as used in the velocity discussion above, the state of equilibrium will be represented by the equation

$$kab = k'cd, \text{ or } ab = \frac{k'}{k}\, cd = Kcd.$$

K is found to be a constant dependent upon the nature of the reacting substances, temperature, pressure, physical state, degree of ionization and so forth. It must be determined by experiment for every reaction and is called the **coefficient of affinity** or the **reaction constant.**

This law was developed by Guldberg and Waage about the

year 1867 and is called the **law of mass action,** or simply the **mass law.**

Illustration.—If potassium nitrate and sulfuric acid are brought together, potassium sulfate and nitric acid are formed, but the reaction is incomplete.

$$\underset{a=\frac{2}{3}}{KNO_3} + \tfrac{1}{2}\underset{b=\frac{2}{3}}{H_2SO_4} \rightleftharpoons \underset{c=\frac{1}{3}}{HNO_3} + \tfrac{1}{2}\underset{d=\frac{1}{3}}{K_2SO_4}.$$

In the equilibrium equation, $a\ b = K\ c\ d$, K has been found to be equal to 4. The equation will therefore be satisfied by making a and b each equal to $\frac{2}{3}$ and c and d each equal to $\frac{1}{3}$. If a gram equivalent each of KNO_3 and H_2SO_4 be used, there will remain $\frac{2}{3}$ of a gram equivalent of each, while $\frac{1}{3}$ of a gram equivalent each of HNO_3 and K_2SO_4 will be formed. The same result is obtained if we start with nitric acid and potassium sulfate. We thus see that the nitrate ion combines with twice as much potassium as the sulfate ion. In a sense then nitric acid is twice as strong as sulfuric acid, or its avidity for the base is twice as great.

Ionization and the Mass Law.—Ionization generally follows the mass law. In the case of strong electrolytes there are irregularities which have not been fully explained. Weak electrolytes obey the law rather rigidly. For the purposes of qualitative analysis we may assume that the law applies in all cases.

A solution of common salt contains undissociated sodium chlorid along with sodium ions and chlorid ions. The relative amounts of these three constituents will depend, other conditions being the same, upon the nature of the substance and the concentration. If K is the **coefficient of ionization,** or **ionization constant** for a given temperature and pressure, and a, b and c represent the concentrations, we shall have according to the mass law.

$$\underset{a}{Na^+} + \underset{b}{Cl^-} \rightleftharpoons \underset{c}{NaCl}, \text{ and } K = \frac{ab}{c}.$$

It is understood that a and b are formed at the expense of c and that as they increase c diminishes. If K is large c must be small and a and b large, that is the substance is strongly ionized;

if K is small, c must be large and a and b small, that is there is little ionization.

When there are just two ions with the same valence, a will be equal to b. If the molecule separates into several ions, the law still applies, but each ion must be taken as a factor. Barium chlorid ionizes as follows:

$$\underset{c}{BaCl_2} \rightleftharpoons \underset{a}{Ba^{++}} + \underset{b}{Cl^-} + \underset{b}{Cl^-}.$$

The equilibrium equation will, therefore, be

$$Kc = abb = ab^2 \text{ and } K = \frac{ab^2}{c} = \frac{a^3}{c}.$$

The mass law as applied to ionization may be stated thus: **The product of the concentrations of the ions divided by the concentration of the undissociated portion is constant for any given electrolyte under given conditions.**

Illustrations.—*a.* A normal solution of sodium chlorid at 18° is 68 per cent. dissociated. The quantities a and b in a liter will, therefore, be 0.68 of one gram equivalent and c will be equal to 0.32 gram equivalent, and the equation becomes,

$$K = \frac{0.68 \times 0.68}{0.32} = 1.445.$$

b. A normal solution of ammonium hydroxid at 18° is ionized to the extent of 0.4 per cent. In this case the equation becomes

$$\underset{0.996}{NH_4HO} \rightleftharpoons \underset{0.004}{NH_4^+} + \underset{0.004}{HO^-}$$

$$K = \frac{0.004 \times 0.004}{0.996} = 0.000016.$$

c. A 0.05 N solution of barium chlorid is about 75 per cent. dissociated. A liter of solution will contain $0.25 \times 0.05 = 0.0125$ gram equivalent of undissociated barium chlorid, $0.75 \times 0.05 = 0.0375$ gram equivalent of barium ions and twice $0.75 \times 0.05 = 0.0375$ equivalent of chlorid ions, and the equation will be

$$K = \frac{0.0375 \times 0.0375 \times 0.0375}{0.0125} = 0.0042.$$

The Degree of Ionization.—The equilibrium equation may be

expressed in terms of the degree of ionization and in this form is useful for certain computations. Let c equal, not the undissociated portion, but the total concentration of the dissolved substance, that is the number of gram equivalents to the liter, and let a equal the fraction of c which is dissociated, while $1 - a$ will represent the undissociated portion. The concentration of each ion then in a binary electrolyte will be equal to $a\,c$ and that of the undissociated portion will be $(1 - a)\,c$. Furthermore, let v represent the volume of the solution which contains one equivalent of the solute, then we will have $v = \frac{1}{c}$ and $c = \frac{1}{v}$. Substituting these values in ionic equilibrium equation we have

$$K = \frac{a^2c^2}{(1 - a)c} = \frac{a^2c}{1 - a} = \frac{a^2}{(1 - a)v}.$$

From the equation, K and c being given, the degree of dissociation, a, is easily calculated. In the illustrations given above in the paragraph on Ionization and Mass Law these substitutions were made. In the case of weak electrolytes the dissociation is so small that $1 - a$ may, without sensible error, be taken as equal to 1 and the equation may be written $K = a^2\,c$ or $\frac{a^2}{v}$ and $a = \sqrt{\frac{k}{c}}$ or $\sqrt{kv}$.

For normal ammonium hydroxid $c = 1$ and $k = 0.000016$, therefore $a = \sqrt{0.000016} = 0.004$, or the solution is 0.4 per cent. ionized.

Effect of Dilution.—The effect of dilution upon the degree of ionization may be computed from the formula of the last paragraph. It will be observed at once that if v decreases or c diminishes a must increase and furthermore that for weak electrolytes a increases as the square root of the increase in volume, or inversely as the square root of the increase in concentration.

Illustrations.—*a.* If a normal solution of sodium chlorid which is 68 per cent. ionized and for which $K = 1.445$ be made half normal by addition of an equal volume of water, we shall have

$$K = \frac{a^2}{2(1 - a)} = 1.445, \text{ or } a^2 = 2.89 - 2.89\,a,$$

from which we find $a = 0.786$. Doubling the volume of the solution or reducing the concentration to one-half has increased the dissociation from 68 to 78.6 per cent.

b. For normal ammonium hydroxid $a = 0.004$ and $k = 0.000016$. If the volume of the solution be quadrupled we shall have

$$K = \frac{a^2}{v} = \frac{a^2}{4} = 0.000016, \text{ or } a = 0.008.$$

Diluting the solution to four times its volume has doubled the dissociation. These results are, of course, only approximate.

Precipitation.—On bringing together in solution two substances which can by interaction form an insoluble, or slightly soluble compound, the compound formed will separate as a precipitate. This process is called precipitation, and is of the greatest importance in qualitative analysis. Precipitation may be the result of various chemical actions, such as union, decomposition, metathesis, hydrolysis, exchange of ionic charges, etc.

Solubility Product.—If a substance formed in a reaction is sparingly soluble, it will soon saturate the solution and begin to precipitate. The process will continue until only that quantity of the substance remains in solution which is necessary to saturation. This saturation quantity is constant and is represented by either member of the dissociation equation $a\ b = K\ c$. Ostwald represented this constant by L and called it the **solubility product** or **ionic product.** In order that a precipitate may be formed the product of the concentrations of the reacting ions must at least be equal to L. If it is above L the precipitate increases; if it is below, the precipitate diminishes, a portion going into solution.

In electrolytes which yield but two ions, a is equal to b and we may write $a^2 = L$. When the solubility is very low, the dissociation is almost complete and c is very small, so that a may be taken to represent the total solubility. In difficultly soluble binary electrolytes, then the solubility will be the square root

of the ionic product, and conversely the ionic product will be the square of the solubility.

Illustration.—Silver chlorid is very slightly soluble in water and the dissolved salt may be regarded as completely ionized. The concentration of the saturated solution has been found to be 0.0000106 moles to the liter. The solubility product is the square of this number, which is 0.000000000112, and the solubility of silver chlorid is 0.0000106 moles or 0.0015 gram to the liter at 18°.

If the substance yields three or more ions, each must be taken as a factor in the solubility product and the computation is more complicated. For discussion of such cases the student is referred to works on Physical Chemistry.

Precipitates.—(*a*) If two ions are present in a solution in quantity exceeding the solubility of their compound, they will unite and a precipitate will fall. Barium ion and sulfate ion unite to form barium sulfate as follows:

$$\underset{a}{Ba^{++}} + \underset{b}{SO_4^{--}} \rightleftharpoons \underset{c}{BaSO_4}.$$

For this reaction the solubility product at room temperature is $a\ b = a^2 = L = 1 \times 10^{-10}$, and the solution so soon becomes saturated that the precipitate falls instantaneously. The precipitation will continue until all the ions are removed except just enough to make the ionic product $a\ b$ equal to L. That which remains will approximately represent a concentration equal to the square root of L, that is 1×10^{-5} moles or 0.00233 gram to the liter.

(*b*) If three kinds of ions are present in approximately equivalent amounts, two of which form sparingly soluble compounds with the third, the two compounds will precipitate approximately in the inverse ratio of their solubility products. If the two compounds are equally soluble, mixed precipitates will be obtained.

Illustration.—Add to 10 cc. 0.1 N $AgNO_3$ a mixture of 10 cc. each of KCl and KI solutions. The precipitate will be practically all AgI. The solubility product is, according to

Goodwin, for AgCl 1.56×10^{-10} and for AgI 0.94×10^{-16}. The ratio of these two numbers is about 1,600,000. The precipitate will, therefore, contain less than one millionth part of its weight of AgCl.

(*c*) If a suspended precipitate be treated with an anion which can form with the metal present a less soluble compound, the precipitate will be gradually changed. The anions with the dissolved portion of the precipitate make a concentration above the solubility of the compound which they form. They therefore unite and precipitate. New ions are supplied by slowly dissolving precipitate. Lead, silver, copper, cadmium and mercury salts are thus converted by sulfid ion into sulfids, and mercuric oxid is changed by iodid ion into mercuric iodid,

$$PbCl_2 + S^{--} \rightleftharpoons PbS + 2Cl^-.$$
$$HgO + 2H^+ + 2I^- \rightleftharpoons HgI_2 + H_2O.$$

The solubility of mercuric oxid is 0.095 gram to the liter, while that of mercuric iodid is only 0.0004 gram to the liter. The mercuric iodid, therefore, readily forms at the expense of the mercuric oxid.

Ionization of Water.—Distilled water has a measurable conductivity which is mainly due to small quantities of dissolved gases and salts. The purest water obtainable has been found to have at 18° a molecular conductivity 0.04×10^{-3}. The maximum molecular conductivity of water if it were wholly ionized would be theoretically 493, the sum of the numbers for H^+ and HO^-. The degree of ionization according to the rule which has been given would be $\frac{0.04 \times 10^{-3}}{493} = 0.8 \times 10^{-7}$. This number also represents the concentration of the separate ions. The conductivity increases as the temperature rises and at 20° the ionic concentration is about 1×10^{-7}. This means that 10^{-7} moles of water are ionized in one liter or one mole in 10,000,000 liters. Water is, therefore, one ten millionth normal with reference to hydrogen and hydroxid ions; or in other words in 10,000,000 liters of water there are 17 grams of hydroxid ions

and one gram of hydrogen ions, or about one gram of water in 555,000,000 grams is dissociated.

In order to convey a better impression of the exceeding small conductivity of water the statement has been made that a column of water one millimeter long offers a resistance to the electric current equal to that of a copper wire of the same diameter as the column of water and 25,000,000 miles long, or long enough to pass around the earth one thousand times! (Kohlrausch and Heydweiller).

Effect of Excess of Ions.—On examining the ionic mass equation it will be seen that if the concentration of either ion is changed, the equilibrium will be disturbed and a reaction will set in which will continue until the ratio of $a\ b$ to c is equal again to K. If a substance is added which yields one of the ions already present, the concentration of this ion will be increased and also the product $a\ b$. In order to preserve the equality, c must increase at the expense of a and b, that is, ions must unite to form the undissociated compound. It is in this way that many reactions are powerfully influenced by the presence of substances which do not seem to take part in the reaction. This principle is of frequent application in explaining the processes of qualitative analysis. The following cases are of special importance:

a. The activity and solvent power of a weak acid are greatly diminished or even reduced to zero by the presence of a highly dissociated salt of the acid. If an acetate be added to a solution containing acetic acid, the excess of acetate ions increases the ionic product $a\ b$ for acetic acid and drives the hydrogen ion back into combination with the acetate ion to form undissociated acetic acid, thus reducing the dissociation of the acetic acid and the number of hydrogen ions in the solution, and therefore reducing or nullifying the activity of the acid.

b. In the same way the presence of the kation of a base diminishes the activity of the base. If ammonium chlorid be added to ammonium hydroxid, the activity of the latter is diminished. The excess of ammonium ions causes a decrease in the dissociation of the hydroxid.

c. The activity of a strong acid may be greatly weakened by the addition of a salt of a weak acid. If to a solution of aluminum phosphate in dilute hydrochloric acid an excess of sodium acetate be added, the phosphate will be precipitated. The acetate ions unite to the hydrogen ions of the hydrochloric acid to form acetic acid which is dissociated but slightly, and thus the concentration of hydrogen ions is reduced while that of the undissociated phosphate is increased until the solubility product of aluminum phosphate is exceeded.

d. Precipitation is made more complete by the presence of either of the ions which combine to form the precipitate. In other words the solubility of a compound is diminished by the presence of an excess of either of its ions. In precipitating barium sulfate, an excess of barium ion or of sulfate ion will raise the product $a\ b$ for barium sulfate above its solubility product L and more ions will unite until equilibrium is restored.

e. Precipitation may be prevented by the presence of an ion which diminishes the dissociation of the precipitant. Iron sulfid formed by the union of ferrous and sulfid ions is sparingly soluble, that is, the solubility product is small. Hydrogen sulfid is but slightly dissociated, but the few sulfid ions which it yields are sufficient to bring the concentration of ferrous sulfid up to the limit of its solubility and there will be a precipitate. If an acid be added, the excess of hydrogen ion diminishes the ionization of the hydrogen sulfid to such an extent that the product of the ionic concentration is less than L. The precipitate, therefore, is not formed, or if it has formed, dissolves. The more soluble manganese sulfid is not precipitated by hydrogen sulfid from neutral solutions because the product of the concentrations of the ions never reaches the solubility product of manganese sulfid, unless the hydrogen ion set free in the reaction is neutralized.

f. Precipitation may be prevented or the precipitate, dissolved by excess of a reagent through the formation of a soluble compound which dissociates yielding a complexion. If ammonium hydroxid be added to a solution of a zinc salt a precipitate of

zinc hydroxid falls, but dissolves on the addition of more of the reagent with formation of the zinc-ammonia salt, which yields the zinc-ammonia ion, $Zn(NH_3)_6^{++}$. See complex ions, page 35.

Illustration.—A normal solution of ammonium hydroxid is about 0.4 per cent. dissociated and the equation is

$$\underset{0.996}{NH_4HO} \rightleftharpoons \underset{0.004}{NH_4^+} + \underset{0.004}{HO^-}$$

$$0.996K = 0.004 \times 0.004$$

$$K = 0.000016$$

If to a liter of this solution a mole of ammonium chlorid be added, it will in dissolving dissociate to the extent of 75 per cent. The concentration of the ammonium ions will be increased by 0.75 gram equivalent, bringing the total concentration to 0.754 equivalent. Introducing this number into the equation and letting x represent the amount by which the dissociation of ammonium hydroxid is reduced, we have

$$(0.996 + x)\ K = (0.754 - x) \times (0.004 - x).$$

Introducing the value of K, 0.000016, and solving for x, we have

$$x = 0.00399 \text{ and } 0.004 - x = 0.00001.$$

Thus the dissociation of the ammonium hydroxid is reduced by the presence of the ammonium chlorid from 0.4 per cent. to 0.001 per cent.

It will be observed that in this example the final degree of dissociation is of the same order with the dissociation constant. This will in general be the case when weak and strong electrolytes of approximately the same concentration and having a common ion are mixed. The degree of dissociation of the weak electrolyte will be approximately equal to its dissociation constant. The dissociation of the strong electrolyte will also be diminished, but only to a small extent.

Example.—The dissociation constant of normal acetic acid is 0.000018 at 18° and the ionization is 0.42 per cent. When mixed with excess of normal sodium acetate the dissociation is reduced to about 0.0018 per cent.

A similar calculation will reveal the effect on precipitation of adding an excess of the precipitant. In the expression for the

solubility product, $a\ b = L$, if one of the ions is increased, the other must be correspondingly diminished. If we let e represent the concentration of the precipitating ion in the precipitant, and y the amount by which the other ion of the precipitate is reduced, we shall have

$$(a + e)\ (b - y) = L \text{ and } (b - y) = \frac{L}{a + e},$$

in which $b - y$ is the reduced solubility.

Example.—The solubility of barium sulfate at 18° is 1×10^{-5}, or 0.00001, and the solubility product is the square of this or 1×10^{-10}, that is for barium sulfate $a\ b = 1 \times 10^{-10}$. If to the saturated solution an equal volume of a normal solution of barium chlorid 70 per cent. ionized be added, the increase of concentration of the barium ion will be 0.7 gram equivalent, or $e = 0.7$. Substituting these values in the equation we have $(0.00001 + 0.7)\ (b - y) = 1 \times 10^{-10}$, or $b - y = 1.43 \times 10^{-10}$, a number which is practically zero.

Complex Ions.—Weak ions may combine with molecules or with other ions to form stronger and more soluble complex ions. It is thus that precipitates are dissolved by certain solutions. In this way silver chlorid reacts with ammonium hydroxid to form silver ammonia kation,

$$AgCl + 2NH_4HO \rightleftharpoons Ag(NH_3)_2^+ + Cl^- + 2H_2O, \text{ or}$$
$$Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2^+.$$

Such complex ions are formed by ammonia, cyanogen, the halogens and several of the acid radicals.

Applying the law of mass action to the above equation, we have

$$\frac{Ag^+ \times NH_3 \times NH_3}{Ag(NH_3)_2^+} = K, \text{ or } \frac{a^3}{1 - a} = K$$

in which a is the fraction of the silver ions which remain uncombined and $1 - a$ the part which enters the complex ion. The constant K for this reaction has been found to be equal to 10^{-7}. Substituting this value in the equation and replacing $1 - a$ by 1, which involves little error since a is very small, we have

$$a^3 = 10^{-7} = \frac{1}{10^7} = \frac{100}{10^9} \text{ and } a = 0.00464.$$

This value of K is called the instability constant of the complex ion. In the presence of chlorid ion less than 0.00001 gram equivalent of silver ions to the liter remain uncombined and therefore chlorid ion should precipitate silver chlorid from this ammoniacal solution. If, however, the ammonia is in excess, the silver ion is driven into combination until the concentration is below the solubility of silver chlorid.

Illustration.—Add sodium hydroxid to silver nitrate solution in slight excess, pour off the liquid from the precipitated silver oxid, add water and pour away two or three times to wash out the sodium hydroxid, then add dilute ammonium hydroxid drop by drop until the silver oxid is just all dissolved. Divide the solution in two parts.

a. To the first portion add sodium chlorid; the precipitate is silver chlorid. Explain.

b. To the other portion add more ammonium hydroxid and then sodium chlorid. No precipitate should fall. Explain.

Hydrolysis.—Many salts in passing into aqueous solution are partially decomposed by the water into acid and base, thus reversing the reaction of neutralization. This effect is due to the ions of water which are always present in slight but measurable quantity. Some salt solutions become acid and others alkalin, while in many cases insoluble compounds are formed. Such action is called **hydrolysis** (decomposition by water). Four cases may arise.

1. If a strongly dissociated salt contains a weak anion, the hydrogen of the water, although present in very small quantity, combines with this anion to form the undissociated acid and the product $a\ b$ for the ions of water is reduced. More water dissociates to restore the product to its constant value and more hydrogen is removed. In this way the hydroxid ion accumulates rendering the solution alkalin. The process continues until the accumulation of hydroxid ions stops the further dissociation of the water. The addition of a base (hydroxid ion) retards or prevents the hydrolysis. The hydrolysis will extend the further

the weaker the anion, that is the lower the degree of ionization of the acid formed.

The following weak anions make alkalin solutions when associated with strong kations: $H_2BO_3^-$, PO_4^{---}, HPO_4^{--}, HS^-, S^{--}, CO_3^{--}, HCO_3^-, CrO_4^{--}, SiO_3^{--}, SO_3^{--}, ClO^-, NO_2^-, CN^-, $C_2H_3O_2^-$.

When these are associated with weak kations the compounds are all insoluble except some of the cyanids and acetates.

The following example illustrates hydrolysis of this kind:

$$K^+, CN^- + H^+, HO^- \rightleftharpoons K^+, HO^- + HCN.$$

If ammonium ion, (ammonium chlorid) is added to this solution, the concentration of the hydroxid ion is diminished because of formation of undissociated ammonium hydroxid and more HCN is formed. This may be observed by noting the increased intensity of the odor.

2. If a salt contains a weak kation, the hydroxid ion of water combines with this kation to form the undissociated base, while the hydrogen ions accumulate because of further dissociation of water rendering the solution acid. The addition of acid hinders or prevents the decomposition. The weaker the kation the greater the degree of hydrolysis.

The following weak kations make acid solutions when associated with strong anions: Ba^{++}, Hg^{++}, Hg_2^{++}, Cu^{++}, Al^{+++}, Cr^{+++}, Fe^{+++}, Mn^{+++}, Sn^{++}, Sn^{++++}, Sb^{+++}, Bi^{+++}, NH_4^+. When these are associated with weak anions they form difficultly soluble compounds and sometimes basic salts.

Hydrolysis of this kind is illustrated by the following example:

$$Fe^{+++}, 3Cl^- + H_2O \rightleftharpoons Fe(HO)Cl_2 + H^+ + Cl^- \text{ or}$$
$$Fe^{+++} + 3H_2O = Fe(HO)_3 + 3H^+.$$

If an anion be added which forms with hydrogen ion a slightly dissociated compound the hydrogen will be removed and the hydrolysis will be increased.

3. If a salt is composed of two weak ions, the dissociation will be greater than in the two previous cases, but the mixture will remain neutral because there is not any large excess of either

hydrogen or hydroxid ions. The reaction may even go to completion, the salt being entirely converted into acid or base.

In this way ammonium silicate in alkalin solution deposits silicic acid,

$$SiO_4^{----} + 4H_2O = H_4SiO_4 + 4HO^-.$$

This principle also explains the formation of many unexpected compounds, especially hydroxids; as for example, in the action of ammonium sulfid or potassium cyanid upon aluminum ions we get hydroxid instead of sulfid and cyanid,

$$2Al^{+++} + 3S^{--} + 6H_2O \rightleftharpoons 2Al(HO)_3 + 3H_2S,$$
$$Al^{+++} + 3CN^- + 3H_2O \rightleftharpoons Al(HO)_3 + 3HCN.$$

4. If the salt is composed of two strong ions there will be no appreciable hydrolysis, because the acid and base which would be formed are both highly dissociated and hence there is no tendency of the ions of the salt to unite to the ions of the water.

The Degree of Hydrolysis.—The hydrolysis in most cases does not reach very far. Decinormal sodium acetate, for example, is only hydrolyzed to the extent of 0.008 per cent. The degree of hydrolysis increases with dilution and with rise of temperature. A few examples are given in the following table:

	Weak anions. 25°			Weak kations. 85°	
0.1N	$NaC_2H_3O_2$	0.008%	0.1N	NH_4NO_3	0.03%
0.1N	$NaHCO_3$	0.06	0.1N	$CuCl_2$	0.3
0.1N	$NaBO_2$	0.84	0.1N	$HgCl_2$	0.5
0.1N	KCN	1.00	0.1N	$PbCl_2$	0.5
0.1N	Na_2CO_3	3.17	0.1N	$Cu(NO_3)_2$	0.6

Hydrolysis follows the law of mass action and the equilibrium equation is as follows:

$$\frac{\text{(Conc. of acid) (Conc. of base)}}{\text{(Conc. of non-hydrolized salt)}} = \frac{a^2c}{1-a} = \text{hydrolytic constant.}$$

A decinormal solution of potassium cyanid at 25° is about 1 per cent. hydrolyzed. The concentrations of the acid and base will be each 0.001 equivalent to the liter and that of the non-hydrolyzed part 0.099, or practically 0.1. Making the substitutions we have:

$$\text{Hydrolytic constant for KCN} = \frac{0.001 \times 0.001}{0.1} = 0.00001.$$

The degree of hydrolysis, when this constant is known, is found from the formula $a^2 c = k$, or $0.1\ a^2 = 0.00001$ and $a = 0.01$.

When the ionization constant of the acid or base is known, the hydrolytic constant and the degree of hydrolysis may be computed from the ionic product for water. For the hydrolysis constant we have $K_h = \frac{k_w}{k_a}$ or $\frac{k_w}{k_b}$ in which k_w is the ionic product of water equal at 25° to 1.2×10^{-14} and k_a and k_b are the ionization constants of the acid and base. For HCN $k_a = 1.3 \times 10^{-5}$ and the value becomes $K_h = \frac{1.2 \times 10^{-14}}{1.3 \times 10^{-5}} = 1 \times 10^{-9}$.

The degree of hydrolysis is given by the formula

$$a = \sqrt{\frac{1}{c} \times \frac{k_w}{k_a}} \text{ or } a = \sqrt{\frac{1}{c} \times \frac{k_w}{k_b}}\ .$$

Substituting the values of k_w and k_a for HCN, we have

$$a = \sqrt{\frac{1}{0.1} \times \frac{1.2 \times 10^{-14}}{1.3 \times 10^{-9}}} = 0.01 \text{ or } 1 \text{ per cent.}$$

For demonstrations of these formulas and full discussion of hydrolysis see Abegg-von Ende's The Electrolytic Dissociation Theory, page 76; Morgan's Physical Chemistry, page 316.

Electrolytic Solution Pressure.—Osmotic pressure may be regarded as the measure of the tendency of a solid to go into solution and may be called **solution pressure.** The solution is saturated when the solution pressure and the osmotic pressure are equal. If a metal be immersed in pure water some of the atoms pass into solution as positive ions, taking their electric charge from the metal and thus rendering it negative. The attraction between the positively charged ions and the negatively charged metal causes the formation of the so-called **double layer** of Helmholtz and a difference of potential arises, as is shown by the movement of the index when the metal is connected with an electroscope. If the negative charge is conducted away from the metal or neutralized by the positive charge, more ions go into solution. The tendency of the metal to pass into solution as ions is called its **electrolytic solution pressure** or **tension,** and equilibrium is established when this pressure is equal to the osmotic pressure of the ions. This pressure may be measured

it atmospheres or in gram-ions to the liter. The osmotic pressure of a solution containing one gram-ion to the liter is 22.4 atmospheres. The electric ionic charge is so very high that equilibrium occurs before weighable quantities of the metal have entered the solution.

When the metal is immersed in pure water the potential difference or the strength of the double layer, will depend solely upon the magnitude of the solution pressure, but if the metal be in solution of one of its salts a modification will occur, due to the metal ions already present. These ions oppose by their osmotic pressure the entrance of other like ions. Three cases may arise:

1. The osmotic pressure of the ions in the solution may be equal to the electrolytic solution pressure of the metal. In this case no double layer will be formed, no difference of potential will arise and no ions will go into solution. Thallium, nickel and cobalt are thus nearly neutral in normal solutions of their salts.

2. If the electrolytic solution pressure is greater than the osmotic pressure of the ions present, ions will pass into solution and the double layer will be formed, but the effect will be smaller than in pure water, because the ionic osmotic pressure is opposed to the solution pressure. Magnesium, zinc, cadmium and iron act in this way in solutions of their salts.

3. If the osmotic pressure of the ions is greater than the solution pressure no ions will go into solution, but, on the contrary, some of the ions will be deposited on the surface of the metal, giving to it their positive electric charge. The metal thus becomes positive and solution negative, the double layer is formed with qualities the reverse of those of the other case, and the potential difference is negative. Lead, mercury, silver and copper act in this way in solutions containing their ions.

In the following table are given for several metals the electrolytic solution pressure in atmospheres and the number of gram-ions to the liter required in order that the osmotic pressure should balance the solution pressure. The solution is supposed to be normal.

Metals	Atmospheres	Gram-ions to liter
Magnesium	1×10^{44}	4.5×10^{42}
Zinc	1×10^{18}	4.5×10^{16}
Aluminum	1×10^{13}	4.5×10^{11}
Iron	1×10^{4}	4.5×10^{2}
Nickel	2×10	1
Lead	1×10^{-3}	5×10^{-1}
Mercury	1×10^{-16}	4×10^{-18}
Silver	2.3×10^{-17}	1×10^{-19}
Copper	1×10^{-20}	5×10^{-22}

One meaning of this table may be illustrated as follows: If zinc is immersed in a solution containing its ions, it will acquire a double layer and a negative charge with all concentrations up to 4.5×10^{16} gram-ions to the liter. Such a concentration is, of course, beyond possibility and zinc will always be negative, in solutions of its ions. Nickel in very dilute solutions will be negative, but in solutions whose concentrations exceed two gram-ions to the liter it will be positive. Copper will be positive in all its solutions until the concentrations are reduced below 5×10^{-22} gram-ions to the liter, a quantity which is below the limits of gravimetric handling.

The solution pressure of zinc is high, while that of copper is low, and a rod of zinc immersed in a copper solution will drive the copper ions back into the metallic state, the process continuing until equilibrium is attained. This will be when the concentrations of the two ions are in proportion of their solution *tensions*,

$$\frac{\text{Concentration of zinc ions}}{\text{Concentration of copper ions}} = \frac{4.5 \times 10^{16}}{5 \times 10^{-22}} = 10^{38}.$$

This may be called the equilibrium constant for zinc and copper. It is so large that practically all the copper is displaced by the zinc.

Indicators.—It is often necessary to know whether a solution is acid or alkalin, that is, whether hydrogen ions or hydroxid ions are present. This information is obtained by the use of a substance which has one color in acid and another in alkaline solution. Such substances are called **indicators.** Those most used with the colors which they exhibit are as follows:

Indicator	Acid	Alkain
Litmus	Red	Blue
Lacmoid	Red	Blue
Methyl orange	Pink	Yellow
Phenolphthalein	Colorless	Red
Turmeric	Yellow	Brown

The action is explained as follows: Methyl orange is a very weak acid whose molecules are pink, while its anions are yellow. When it is dissolved in water it undergoes a sufficient dissociation for the anions to give the solution a yellow color not changed by the addition of an alkali which tends rather to increase the dissociation. On the addition of the acid the excess of hydrogen ions drives the indicator back to the molecular condition and its pink color appears. This is a good indicator for strong acids and weak bases.

Phenolphthalein is a still weaker acid whose anions have an intensely reddish purple color, while its molecule is a pale yellow so faint that its solution appears colorless. It is so slightly dissociated that no color is observed and an added acid tends still more to restrict the dissociation. On addition of an alkali, however, the hydroxid ion combines with the hydrogen ion to form water and further dissociation causes the red color of the anion to appear. This is a good indicator for weak acids and strong bases. It must be dissolved in dilute alcohol.

Any indicator may be used when it is simply desired to know whether the solution is acid, alkalin or neutral. To find a sharp end reaction in neutralization, discretion must be exercised in the choice of an indicator. The following rules will be uselful:

1. For strong acid and strong base—any indicator.

2. For strong acid and weak base—stronger acid indicator (methyl orange).

3. For weak acid and strong base—weakest acid indicator (phenolphthalein).

4. For weak acid and weak base—no indicator gives a sharp end reaction.

The color changes in indicators have recently been otherwise explained. For the new theories the student is referred to the chemical Journals.

Chapter V

REACTIONS

Reactions are used both for separation and identification. For separation those are commonly selected which produce precipitates. For identification we may use any of the properties or reactions of the compound formed or under investiagtion. Certain characteristic properties or reactions are known as **final** or **confirming** tests.

The two agents which are most efficient in bringing about reactions or in assisting them are heat and water. We may therefore distinguish two classes, **Dry Reactions,** those in which heat is applied to the dry substance with or without the aid of chemical reagents; and **Wet Reactions,** those in which the change is brought about in aqueous solution with or without the aid of heat.

The effect of heat upon the velocity of a reaction and the influence of water as a solvent and ionizing agent has been discussed in the chapter on Solutions. Even dry reactions are greatly assisted by the catalytic action of the small amount of moisture present. Absolutely dry substances do not seem to be able to begin to act.

In both dry and wet reactions there may be oxidation or reduction from which actions important information may be obtained.

OXIDATION

Oxidation primarily means the increase of the relative amount of oxygen in the molecule. It may be effected by adding oxygen or by taking away hydrogen. Ferrous oxid heated in the air becomes ferric oxid, and carbon monoxid burns to carbon dioxid,

$$2FeO + O = Fe_2O_3, \quad CO + O = CO_2.$$

Vapor of methyl alcohol mixed with air is oxidized by red-hot platinum wire to formic aldehyde by removal of hydrogen,

$$CH_3OH - 2H = CH_2O, \text{ or } CH_3OH + O = CH_2O + H_2O.$$

The term oxidation is also extended to mean the increase of the relative amount of any element which may represent the oxygen that is an increase of valence. Ferrous chlorid is oxidized by nitric acid to ferric chlorid, and sufurous acid on exposure to the air gradually becomes sulfuric acid.

An indirect oxidizing agent is one which, although containing no oxygen itself, is able to set oxygen free from something else. The halogens in the presence of water are such agents. They take hydrogen from water to form the haloid acid and set the oxygen free, which in the nascent state is a powerful oxidizer.

The principal oxidizing agents are:

1. Oxygen,
2. The halogens,
3. Nitric acid,
4. Hydrogen peroxid,
5. Sodium peroxid,
6. Copper oxid,
7. Potassium chlorate,
8. Potassium permanganate,
9. Potassium dichromate,
10. Potassium nitrate.

REDUCTION

Reduction is the opposite of oxidation and means decrease of the amount of oxygen, or increase of the amount of hydrogen, or lowering of the valence. If ferric oxid is heated with carbon it is first reduced to ferrous oxid and then to metallic iron.

$$Fe_2O_3 + C = 2FeO + CO, \qquad FeO + C = Fe + CO.$$

We speak also of reducing nitrates to nitrites, ferric ion to ferrous ion, and so forth.

The more important reducing agents are:

1. Nascent hydrogen,
2. Carbon,
3. Metals,
4. Hydrogen sulfid,
5. Sulfurous oxid,
6. Stannous chlorid,
7. Hydriodic acid,
8. Sodium carbonate,
9. Oxalic acid,
10. Alcohol,
11. Potassium cyanid.

Oxidation and reduction always go together. The one involves the other. When hydrogen reduces copper oxid, it itself is oxidized to water, and when nitric acid oxidizes ferrous to ferric ion, it is reduced to nitrous acid. Nitrous acid in the presence of a strong oxidizing agent is a reducer; in the presence of a strong reducing agent is an oxidizer.

The Bunsen flame or the blow-pipe flame may be used for oxidation or reduction. In general the outer portion of the flame where there is an excess of air has an oxidizing action, while the inner portion where there is an excess of gas has a reducing action.

In the case of ions oxidation means increase of positive or decrease of negative electric charge, while reduction is just the reverse. This principle is illustrated by the following ionic equations:

1. $Fe^{++} + Cl_2 = 2Fe^{+++} + 2Cl^-$.
2. $2Fe(CN)_6^{----} + Cl_2 = 2Fe(CN)_6^{---} + 2Cl^-$.
3. $2MnO_4^{--} + H_2O_2 = 2MnO_4^{-} + 2HO^-$.
4. $2Fe^{+++} + S^{--} = 2Fe^{++} + S$.

In the first reaction ferrous is oxidized to ferric ion while molecular chlorin is reduced to chlorid ion. In the second reaction ferrocyanid ion is oxidized to ferricyanid ion, the negative electric charge being diminished while at the same time the valence of iron is increased. In No. 3 manganate ion becomes permanganate ion by lowering of ionic charge and hydrogen peroxid is reduced to hydroxid ion. In No. 4 ferric is reduced to ferrous ion while sulfid ion is oxidized to sulfur.

ELECTRIC PHENOMENA OF OXIDATION AND REDUCTION

Oxidation and reduction may result from the passage of an electric current through an electrolyte, and on the other hand when these actions occur an electric current is produced. These facts may be verified by experiments like the following:

1. Oxidation and reduction by means of the electric current.

a. Place a small beaker within a large one and add a solution of ferric chlorid until the small beaker is just covered. Lower the positive electrode of a battery into the larger beaker and the negative electrode into the smaller one and pass current for a few minutes. Remove with a pipet from the vicinity of the kathode a little of the solution and test it for ferrous ion with a fresh solution of potassium ferricyanid. Ferric has been reduced to ferrous ion.

b. Empty the beakers, wash well and fill with a solution of ferrous chlorid freshly prepared by dissolving iron wire in dilute hydrochloric acid. Introduce the electrodes with the anode in the smaller beaker, pass the current, remove with the pipet a portion from near the anode and test for ferric ion with ammonium thiocyanate. Ferrous ion has been oxidized to ferric ion.

Oxidation takes place at the positive electrode and reduction at the negative electrode.

2. Electric current from oxidation and reduction.

a. Place in one small beaker a solution of ferric chlorid and in another a solution of sodium chlorid and connect the two beakers with a small inverted U-tube filled with sodium chlorid solution. Introduce platinum electrodes and connect with a sensitive galvanometer, the ferric solution with a positive pole. Note whether a current passes. Add a little potassium iodid to the beaker containing the ferric chlorid and note whether the current is made stronger.

b. Repeat the experiment with ferrous sulfate solution freshly prepared by dissolving iron wire in dilute sulfuric acid, using bromin water instead of the potassium iodid. Note the direction of the current.

DRY REACTIONS

Dry reactions are used in preliminary tests, in confirming the presence of certain metals and in the examination of certain minerals. The principle operations follow.

Heating in the Air.—The substance is heated gently or strongly in a porcelain capsule, or on platinum foil. The result may be combustion, oxidation, sublimation, volatilization, change of color, decomposition, fusion with or without decomposition.

Heating Away from the Air.—The substance is heated in a test-tube. It will undergo the same changes as when heated in the air, but with less oxidation. An oxidizing agent or a reducing agent or a flux may be placed in the tube along with the substance modifying the action accordingly.

Heating on Charcoal.—The substance is placed in a little cavity in a stick of charcoal and heated in the blow-pipe flame. The oxidizing or the reducing flame may be used, but since charcoal is a reducing agent the operation is specially adapted to reductions. Many metals may thus be set free from their compounds.

Bead Reactions.—Important reactions are obtained by forming beads of certain fluxes, such as borax, $Na_2B_4O_7,10H_2O$, or salt of phosphorus (microcosmic salt), $NaNH_4HPO_4,4H_2O$. A piece of fine platinum wire about 5 centimeters long is fused into the end of a glass tube. A small loop made in the end of the wire is heated to redness and dipped into the flux, then held in the Bunsen flame. The dipping should be repeated until the loop is full and the heating continued until the bead is transparent. If the bead is not colorless, a new one should be formed. A very small portion of the powdered substance to be tested is taken by bringing it into contact with the moistened bead and is brought in the Bunsen or blow-pipe flame. Either oxidation or reduction may be obtained according to the kind of flame used. Several of the metals give characteristic colors to the bead by which they are identified.

Fusion.—A substance may be fused in order to bring about certain decompositions, but generally the fusion is carried out with a flux for the purpose of converting insoluble into soluble compounds. The usual flux is a mixture of sodium and potassium carbonates in molecular proportions. This mixture melts at a lower temperature than either of the compounds separately. If oxidation is desired, the flux is a mixture of sodium carbonate and potassium nitrate; if the substance is to be reduced, the flux is sodium carbonate and potassium cyanid.

The fusions needed in qualitative analysis can usually be effected on a piece of platinum foil or on a crucible lid.

Flame Coloration.—Certain metals give characteristic colors to the Bunsen flame. Acid solutions are best adapted to this operation and the substance is brought into the flame on the platinum wire as in bead reactions. Sodium colors the flame yellow,

potassium violet, lithium crimson and so forth. The sodium color hides the other color, but may be cut off by viewing the flame through a blue glass.

Spectrum.—Most of the chemical elements have characteristic spectra by which they may be identified even in the presence of one another. White light coming from incandescent solid bodies give a continuous spectrum, that is, the bands of color are continuous without break. An element gives a discontinuous spectrum, that is a spectrum consisting of one or more colored lines having a fixed location in the spectrum. Sunlight gives what is called the absorption spectrum, crossed by numerous dark lines corresponding to the discontinuous spectra of the elements. A gas or vapor absorbs the same light it emits.

Flame Spectra.—Substances which are volatile may be examined in the Bunsen flame. The spectroscope is arranged, best in a darkened room, with the flame a few centimeters in front of the slit. A platinum wire is dipped into the solution to be tested, or the salt moistened with hydrochloric acid, and brought into the flame. The yellow sodium line will always be visible and its position is to be noted on the scale, or the scale may be moved until the line corresponds with some number, say 50. If the instrument has a reflecting prism, the spectrum of the known substance may be placed alongside of that of the unknown and thus the identification is made easy.

Spark Spectra.—For substances not volatile in the Bunsen flame the spark spectra may be used. The substance is brought into the spark between platinum terminals connected with an induction coil.

Absorption Spectra.—For absorption spectra white light is passed through gases or solutions and then observed in the spectroscope.

WET REACTIONS

Wet reactions are those which are brought about in aqueous solutions, often with the help of acids, alkalis or salts, and

with or without heat. Schemes of qualitative analysis are primarily based upon wet reactions because it is in solutions that reactions take place most freely and most completely.

Many of the phenomena of wet reactions have been given under the head of Solutions, and the operations have been described under Separations.

REAGENTS

A reagent is used in qualitative analysis to bring about with an unknown substance a reaction which shall result in the formation of a known substance. For example, if I add hydrochloric acid to a solution and get a white precipitate which is soluble in ammonium hydroxid, I am safe in concluding that a silver salt was present, because silver chlorid is the only substance soluble in ammonium hydroxid which could be formed under the conditions.

The reagents most used are the acids, the alkalis, salts of the alkali metals, ammonium hydroxid, ammonium salts, hydrogen sulfid, ammonium sulfid, and so forth. Besides these there are many special reagents, such as salts of barium, lead, tin, silver and mercury.

Reagents are best used in solutions of known strength. The normal strength or some multiple of it is most convenient.

A table of reagents and a description of the method of preparing them will be found in Part 5.

PART II

BASIC ANALYSIS

Properties and Reactions of the Kations or Positive Elements and the Method of their Separation and Identification

Chapter VI

GROUP 1. SILVER GROUP

Silver, Mercurous Mercury, Lead

Properties and Reactions of the Metals and Ions of Group 1

SILVER

Metallic Silver.—Silver is a white, lustrous metal, malleable, very ductile, in hardness between gold and copper, melting-point 954°, specific gravity. 10.5. It dissolves in nitric acid and in hot sulfuric acid, but not in alkalis. It is blackened by hydrogen sulfid.

Silver Compounds.—Silver forms binary compounds with the negative elements as well as salts with many of the acids. Only a few of its compounds are soluble in water. See Table of Solubilities.

Silver Ions.—Silver forms one simple kation, Ag^+, colorless, univalent and weakly positive. It forms with ammonia and cyanogen the complex ions $Ag(NH_3)_2^+$ and $Ag(CN)_2^-$.

Silver Reactions.—The student should bring about the more important reactions indicated throughout the book and carefully observe and test the results. He should study the formulas and equations and the applications of the laws of equilibrium and mass action until all are thoroughly understood. One cubic centimeter of a solution or a small portion of a precipitate should be transferred to a test-tube or beaker and the reagent applied drop by drop to slight excess (except when excess is called for).

Small quantities will almost always give the best indications. The tests may generally be applied without filtering, the supernatant liquid being poured away and the precipitate washed two or three times by decantation. The precipitation is best made in a test-tube and after the washing the tube may be left one-third full of water with the suspended precipitate. Portions for testing are removed by means of a glass tube used pipet fashion. Each precipitate should be tested for solubility with acids, alkalis, ammonium hydroxid, potassium cyanid and so forth.

The following experiments will illustrate the method which may be pursued with each ion. The test may be varied indefinitely, but should be such as to exhibit the properties and reactions mentioned for each ion under the head of each reagent.

1. To 5 cc. silver nitrate solution add dilute hydrochloric acid drop by drop with shaking as long as precipitate forms. What is the precipitate? How much silver ion will remain in solution? How much if HCl be added in excess? The solubility product for AgCl is 1.12×10^{-10} and the solubility is therefore 1.06×10^{-5} gram equivalent, or 0.0016 gram to the liter at 20°. Explain.

2. Pour off the liquid from the precipitate and wash two or three times by decantation. Remove small portions with a pipet to another tube so as to get a few flakes of the precipitate for each experiment. Test for solubility with the following and give the results: HNO_3, H_2SO_4, HCl, KHO, NH_4OH, KCN, $Na_2S_2O_3$. What compounds and ions are formed with the last three?

3. Add to a bit of the silver chlorid concentrated HCl and warm. Does it dissolve? What is formed?

4. Add to a portion of the silver nitrate solution sodium hydroxid. What is the precipitate? Write the equation. Wash by decantation then add drop by drop dilute ammonium hydroxid until the precipitate just dissolves. What is formed? Write the equation. What is the instability constant in this reaction? See Complex Ions, Chapter III.

a. To a portion of this solution add sodium chlorid. Why is there a precipitate and what is it? Why is the quantity of the precipitate small?

b. To another portion of the solution add more ammonium hydroxid and then sodium chlorid. Why is there now no precipitate?

5. To a portion of the silver nitrate solution add hydrogen sulfid. What is the precipitate? Write the ionic equaton. How much silver ion remains in solution? See below for solubility of silver sulfid. Wash twice by decantation and test separate portions for solubility in acids and alkalis. Treat a portion with hot nitric acid. What results?

6. Add to silver nitrate solution potassium chromate and wash by decantation. What is the precipitate? Write the equation in ions. Test separate portions for solubility in acids, alkalis and ammonium hydroxid. Why does it not dissolve in HCl? What is formed? What results when ammonium hydroxid is used?

7. Dip in silver nitrate solution a bright strip of copper. Why is the silver deposited on the copper? Write the ionic equation. Find the equilibrium constant. See Electrolytic Solution Pressure, Chapter III.

Let the student carry out similar experiments with solutions of mercury and lead, as well as of the metals of the other groups, being guided by those properties and reactions which are mentioned in the text.

Use for the following reactions 0.05 N silver nitrate solution, equivalent 170. Dissolve 8.5 grams $AgNO_3$ in one liter of distilled and freshly boiled water.

A star indicates the more important and characteristic reactions.

*1. **Soluble chlorids** (chlorid ion) precipitate white silver chlorid, AgCl, which darkens in the light because of decomposition which sets silver free. It is insoluble in dilute acids and in alkalis, soluble in warm concentrated hydrochloric acid, in ammonium hydroxid and in alkali cyanids and thiosulfates. With

ammonium hydroxid the complex silver ammonia kation is formed,

$$AgCl + 2NH_4HO = Ag(NH_3)_2^+ + Cl^- + 2H_2O.$$

The silver chlorid is reprecipitated on neutralizing with HCl. With cyanid and thiosulfate ions the reactions are as follows:

$$AgCl + 2K^+ + 2CN^- \rightleftharpoons Ag(CN)_2^- + 2K^+ + Cl^-$$

$$AgCl + 2Na^+ + S_2O_3^{--} \rightleftharpoons Na^+, Cl^- + Na^+, AgS_2O_3^-.$$

The actions of these solvents may be explained as follows: Silver chlorid in contact with water is very slightly dissolved and ionized. When the cyanid ion is introduced the silver ion unites to it to form the more stable and quite soluble silver cyanid ion and the concentration of the silver ion is diminished. More silver chlorid then passes into solution and ionizes to preserve the equilibrium, or to keep the ionic concentration up to the solubility. Thus by continued formation of the complex ion the silver chlorid is all dissolved.

A liter of water at 20° dissolves 0.0016 gram silver chlorid.

The solution is concentrated hydrochloric acid probably contains the compound $HAgCl_2$, from which the silver chlorid is precipitated on dilution.

2. **Soluble bromids and iodids** (bromid and iodid ions) precipitate bromid and iodid of silver which have properties very similar to those of the chlorid. They are less soluble than the chlorid and less stable, being more easily decomposed by light. The iodid is only slightly soluble in ammonium hydroxid. A liter of water dissolves at 20° 0.000084 gram of AgBr and 0.0000028 gram of AgI. Their action with the solvents is similar to that of AgCl given in 1 on preceding page.

*3. **Soluble cyanids** (cyanid ions) precipitate white silver cyanid, AgCN, soluble in alkali cyanids and in ammonium hydroxid with formation of complex ions as explained above, insoluble in dilute acids, decomposed by concentrated acids. Water dissolves at 20° 0.00022 gram to the liter.

*4. **Alkali hydroxids** (hydroxid ions) precipitate unstable white silver hydroxid, AgHO, which immediately turns brown or

black because of decomposition and formation of silver oxid,

$$Ag^+ + HO^- \rightleftharpoons AgHO, \qquad 2AgHO = Ag_2O + H_2O.$$

Silver oxid is soluble in acids, in ammonium hydroxid, in potassium cyanid and in many salts; converted by hydrochloric acid into silver chlorid; insoluble in alkali hydroxids. It dissolves in water at 20° 0.021 gram to the liter.

*5. **Ammonium hydroxid** added drop by drop throws down silver oxid as above, soluble in excess of the reagent. The compound, $Ag(NH_3)_2HO$, called silver ammonia hydroxid, is formed and at once dissociates, yielding the complex ion $Ag(NH_3)_2^+$, or Ag—NH_3—NH_3—. This compound dissolves in water about 0.05 gram to the liter.

5. **Alkali carbonates** (carbonate ions) give a yellow precipitate of silver carbonate, Ag_2CO_3, unstable, decomposing when heated into Ag_2O and CO_2. Silver carbonate dissolves readily in nitric, sulfuric and acetic acids and in ammonium hydroxid, is converted by hydrochloric into AgCl, and dissolves in water at 20° 0.017 gram to the liter.

*6. **Hydrogen sulphide** precipitates black silver sulfid, Ag_2S, insoluble in water, in dilute acids, in alkali hydroxids and in ammonium hydroxid, soluble in hot nitric acid with separation of sulfur. Water dissolves less than 0.000001 gram to the liter.

7. **Phosphate, Arsenate and Arsenite ions** precipitate the corresponding normal silver salts, all insoluble in water, soluble in acids except haloid acids. Water dissolves at 20° 0.0065 gram Ag_3PO_4 to the liter.

8. **Potassium chromate** precipitates red silver chromate, Ag_2CrO_4, soluble in acids except haloid acids, in ammonium hydroxid, in alkali chromates, and in water 0.025 gram to the liter.

*9. **Metallic copper** displaces silver from solution, the latter forming a metallic mirror on the surface of the former. Silver is also displaced by zinc and other metals which precede it in the electrochemical series of kations.

10. **Dry Reactions.**—With fusion mixture of sodium and potassium carbonates silver compounds give a metallic bead in the reducing flame on charcoal.

MERCURY

Metallic Mercury.—Mercury is lustrous and silver white, the only metal liquid at ordinary temperature It has specific gravity 13.59, boils at 358° and freezes at —39.4°. It does not tarnish in the air and is not attacked by hydrochloric acid. It dissolves in sulfuric and nitric acids without evolution of hydrogen. Why?

Compounds of Mercury.—There are mercuric and mercurous compounds. In the former the valence of the mercury is two while in the latter it is apparently one (pseudo-monad though the formulas are usually so written as to exhibit the bivalency. Only a few mercuric compounds are soluble in water and mercurous compounds are generally insoluble.

Ions of Mercury.—Mercury furnishes two simple ions, mercuric Hg^{++} and mercurous Hg_2^{++}, both bivalent, basic, colorless and poisonous. The first is the more stable, the second being easily changed into it. Mercuric compounds are readily reduced to mercurous compounds and these to metallic mercury. Stannous chlorid, for example, reacts as follows:

$$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4.$$
$$Hg_2Cl_2 + SnCl_2 = 2Hg + SnCl_4.$$

Mercurous Reactions.—Use 0.05 normal solution of mercurous nitrate, $Hg_2(NO_3)_2{,}2H_2O$, equivalent 280. Dissolve 14 grams of the crystallized salt in 100 cc. of water to which 25 cc. of concentrated nitric acid have been added, make up to one liter and add a drop of mercury.

*11. **Soluble halids** (chlorid, bromid, iodid ions) precipitate mercurous halids insoluble in water and in dilute acids. The chlorid is white, the bromid yellow and the iodid green. The iodid is unstable darkening in the light. A liter of water at 20° dissolves 0.002 gram of Hg_2Cl_2, 0.000039 gram Hg_2Br_2, and 0.0000002 gram Hg_2I_2. The last is one of the least soluble of all substances.

Mercurous chlorid dissolves in hot strong acids, slightly in ammonium and alkali chlorids, and with nitric acid forms mercuric chlorid and nitrate. Chlorin oxidizes it to mercuric chlorid and ammonium hydroxid converts it into black mercurous ammonium chlorid, Hg_2 replacing two hydrogen atoms in the ammonium radical. This last is a characteristic reaction for mercurous compounds,

$$Hg_2Cl_2 + 2NH_4HO \rightleftharpoons Hg_2NH_2Cl + NH_4Cl + 2H_2O.$$

*2. **Cyanid ion** precipitates the gray metal since mercurous cyanid decomposes at once into mercuric cyanid and mercury.

*3. **Alkali hydroxids** give a black precipitate of mercurous oxid, Hg_2O, insoluble in dilute acids, in alkalis and in ammonium hydroxid, soluble in nitric acid and in warm acetic acid, converted by hydrochloric acid into mercurous chlorid, decomposed by heat or light into mercury and mercuric oxid.

*4. **Ammonium hydroxid** precipitates the black mercurous ammonium salt soluble in excess and in aqua regia.

*5. **Hydrogen sulfid** gives a black precipitate which is a mixture of mercuric sulfid and mercury, soluble in aqua regia. Mercurous sulfid does not seem to form.

6. **Ammonium sulfid** gives the same precipitate as hydrogen sulfid, but with a smaller proportion of mercury, since polysulfids convert it into its sulfid.

*7. **Stannous chlorid** reduces mercurous ion to mercury, as has already been explained.

*8. **Copper, zinc** and **iron** displace mercury (both mercurous and mercuric) from its solutions, the mercury becoming molecular and the other metal taking the electric charge,

$$Cu + Hg_2^{++} = Cu^{++} + 2Hg.$$

A strip of copper dipped in a mercury solution receives a white coating of copper amalgam. On heating the strip in a tube the mercury sublimes and condenses on the glass.

9. **Dry Reactions.**—Mercury compounds may generally be decomposed by heating in a test-tube. If heat alone is not sufficient fusion mixture may be used.

LEAD

Metallic Lead.—Lead is a bluish white metal which tarnishes rapidly in the air, becoming coated with the suboxid, Pb_2O, which protects it from further oxidation. It is soft enough to mark on paper and its tenacity, elasticity, ductility and malleability are low. It melts at 325° and its specific gravity is 11.37. It dissolves poorly in concentrated acids, freely in dilute nitric acid.

Lead Compounds.—Lead forms many compounds, both binary and ternary, a few soluble, the rest insoluble in water, all easily reduced by sodium carbonate. Lead compounds dissolve in acids to form lead salts and in alkalis to alkali plumbites and plumbates.

Lead Ions.—Lead forms one well defined elemental ion, Pb^{++}, colorless, active, bivalent and weakly positive. With strong alkalis the lead hydroxids are acidic and form plumbites and plumbates the anions being PbO_2^{--} and PbO_3^{-+-} or PbO_4^{----}.

Lead Reactions.—Of the salts of lead only the nitrate, chlorate and acetate are readily soluble in water.

Use for the reactions 0.05 N solution of lead acetate, $Pb(C_2H_3O_2)_2,3H_2O$, equivalent 189.5. Dissolve 9.5 grams in one liter of water and add a little acetic acid to prevent formation of lead carbonate.

*1. **Soluble halids** precipitate the chlorid, bromid and iodid of lead, the first two white, the last yellow, soluble in alkali hydroxids and in concentrated acids except sulfuric, slightly soluble in water. If dilute hydrochloric acid be added to a saturated solution of lead chlorid, the excess of chlorid ion causes precipitation, but the precipitate dissolves on further addition of acid. A liter of water dissolves at 15° of lead chlorid 9.09 grams, of lead bromid 7.31 grams. of lead iodid 0.61 gram.

2. **Cyanid ion** precipitates white lead cyanid, Pb(CN)2, insoluble in excess, soluble in alkalis and in acids and in water very slightly.

*3. **Alkali hydroxids** precipitate white lead hydroxid, $Pb(HO)_2$, which dissolves in excess of the reagent to form alkali plumbites and in acids to lead salts:

$$Pb^{++} + 2HO^- = Pb(HO)_2,$$
$$Pb(HO)_2 + 2HO^- = PbO_2^{--} + 2H_2O,$$
$$Pb(HO)_2 + 2H^+ = Pb^{++} + 2H_2O.$$

It dissolves in water 0.017 gram to the liter.

4. **Ammonium hydroxid** precipitates lead hydroxid scarcely soluble in excess of the reagent.

5. **Carbonate ions** (alkali and ammonium carbonates (precipitate white basic lead carbonate of varying composition, soluble in alkalis and in acids, except sulfuric acid and some others, and in water 0.0011 gram to the liter, insoluble in ammonium hydroxid.

*6. **Potassium chromate** gives a yellow precipitate of lead chromate, $PbCrO_4$, soluble with some difficulty in acids, easily in alkalis, and in water 0.0002 gram to the liter. It dissolves in nitric acid to lead nitrate and in alkali hydroxids to alkali plumbites.

Potassium dichromate acts like potassium chromate.

*7. **Hydrogen sulfid** precipitates black lead sulfid, PbS, insoluble in cold dilute acids, in alkalis and in ammonium hydroxid. It dissolves in hot nitric acid, forming lead nitrate and liberating sulfur, while at the same time some of the lead sulfid is oxidized to lead sulfate. Concentrated nitric acid converts the whole of the lead sulfid into lead sulfate. It dissolves in water 0.0009 gram to the liter.

Ammonium sulfid acts like hydrogen sulfid.

*8. **Sulfate ions** (sulfuric acid and soluble sulfates) give a white precipitate of lead sulfate, $PbSO_4$, slightly soluble in water, less so in presence of dilute sulfuric acid or of alcohol. Its diminished solubility in presence of sulfuric acid is in accordance with the law of mass action. The excess of sulfate ions increases the ionic product and to restore equilibrium the number of lead ions must diminish and the precipitation is rendered more complete. Lead sulfate is more or less soluble in alkali

hydroxids, in hot hydrochloric acid, in strong sulfuric acid, in sodium thiosulfate and in ammonium salts, especially the acetate. It dissolves in water at 20° 0.042 gram to the liter.

9. **Phosphate ion,** PO_4^{---}, precipitates white normal lead phosphate, $Pb_3(PO_4)_2$, soluble in acids, in alkalis, and in water 0.000135 gram to the liter at 20°, or 1 part in 7,400,000.

10. **Zinc, tin** and **iron** displace lead from its solutions while lead displaces mercury, silver, gold and platinum.

11. **Dry Reactions.**—In the reducing flame on charcoal, with or without fusion mixture, lead compounds are reduced to metallic lead, the coal receiving a yellow incrustation of lead oxid, PbO.

ANALYSIS OF THE SILVER GROUP

Separation and Identification of the Metals and Ions of Group 1

Metals whose chlorids are insoluble in dilute hydrochloric acid.

Metals: Silver, mercurous mercury, lead.

Ions: Ag^+, Hg_2^{++}, Pb^{++}.

Group reagent. Dilute hydrochloric acid (chlorid ion.)

Principle.—The ions of this group react with the chlorid ion to form molecular chlorids which are insoluble in water and in dilute acids. They are therefore precipitated by solutions containing chlorid ions, that is by solutions of soluble chlorids.

The Group Reagent.—Any soluble chlorid will serve as reagent for the group. Hydrochloric acid is used because the hydrogen ion holds in solution the ions of the other groups and does not interfere with the subsequent treatment of the filtrate for them.

The Precipitate.—The precipitate may contain silver chlorid, AgCl, mercurous chlorid, Hg_2Cl_2, and lead chlorid, $PbCl_2$, all white. Lead belongs to Group 2, but appears here because its chlorid is not very soluble. The precipitate is formed by simple union of ions with disappearance or neutralization of electric charges,

(a) $Ag^+ + Cl^- \rightleftharpoons AgCl$ (b) $Hg_2^{++} + 2Cl^- \rightleftharpoons Hg_2Cl_2$

(c) $Pb^{++} + 2Cl^- \rightleftharpoons PbCl_2$.

When we say that a substance is insoluble, we mean that the

quantity dissolved is inappreciable or quite small. The quantities remaining in solution after precipitation vary exceedingly. Of the precipitates of this group, for example, one liter of water at 20° will dissolve 11 grams of lead chlorid, 0.0015 gram silver chlorid and 0.002 gram mercurous chlorid. Unless the substance is present in quantity exceeding its solubility there will be no precipitate.

Precipitates Not Belonging to Group 1.—The addition of hydrochloric acid may cause precipitation of substances not belonging to Group 1 as follows:

1. Oxychlorids from alkalin solutions of antimony, bismuth and tin.
2. Antimonic and stannic acids.
3. Cyanids from complex cyanids.
4. Sulfur from ammonium and alkali sulfids and thiosulfates.
5. Sulfids from thiosalts.
6. Boric acid from borates.
7. Silicic acid from silicates.

The oxychlorids, the cyanids (except silver cyanid) and boric acid dissolve in excess of hydrochloric acid with heat; sulfur may be dissolved out with carbon disulfid; the sulfids will generally be colored; the silicates, antimonic acid and stannic acid may be identified as explained elsewhere. In general, a precipitate which does not dissolve in hydrochloric acid and is neither dissolved nor blackened by ammonium hydroxid may be regarded as foreign to the group.

The Analysis.—The substance to be analyzed must first be brought into solution. If it is found not to be soluble in water, it must be systematically treated as directed in Chapter XIV.

Better results will generally be obtained by using small portions of the solution and much time will be saved in filtering by avoiding bulky precipitates. A preliminary test should be made at the beginning of every operation in order that the final result may be anticipated. If this test should give negative results the operation is to be omitted with the main solution.

1. To a portion of the solution add dilute hydrochloric acid drop by drop with shaking until no further precipitate seems to form. Avoid much excess of the acid. Warm gently, cool, filter and wash with cold water, to which a drop or two of hydrochloric acid has been added. The wash water may be thrown away, but must first be tested for lead. Add a drop of the acid to the filtrate to see if the precipitation is complete. If it is not add more acid and filter again.

The filtrate may contain the ions of the other groups along with hydrogen ion and chlorid ion. Use it for Group 2.

If there is no precipitate, no metal of this group is present. Pass on to Group 2. See page 60 for precipitate not belonging to the group.

A precipitate may be AgCl, Hg_2Cl_2, $PbCl_2$. Treat as below.

2. Pour over the precipitate of 1 on the filter 20 cc. of boiling water, catch in a beaker and pour through again. Lead chlorid dissolves.

The filtrate contains the lead ion if lead is present.

The residue is silver chlorid or mercurous chlorid, or both.

3. As the filtrate of 2 cools white crystals of $PbCl_2$ separate if lead is present in sufficient concentration. Confirm by adding to one portion of the filtrate potassium chromate (chromate ion) and to another a soluble sulfate (sulfate ion). A yellow precipitate of lead chromate or a white one of lead sulfate, both soluble in sodium hydroxid (difference from barium), proves the presence of lead.

4. If lead is present, continue the washing of the residue of 2 until a drop of the filtrate taken from the end of the funnel on a watch-glass gives no precipitate or a very faint one with sulfuric acid. If lead is absent, this washing is omitted. If there is no residue, silver and mercury are absent.

Treat the washed residue, or the washed precipitate of 1 if lead is absent, on the filter with a little dilute ammonium hydroxid, pouring it through two or three times. Silver chlorid goes into solution as silver ammonia chlorid, $Ag(NH_3)_2Cl$, which ionizes into the silver ammonia ion, $Ag(NH_3)_2^+$, and chlorid ion,

Cl^{-}, while mercurous chlorid is changed into black mercurous ammonium chlorid, Hg_2NH_2Cl, with some free mercury, and remains on the filter undissolved. If mercury is not present, the entire precipitate dissolves; if silver is not present, the residue blackens without dissolving. If mercury is absent and there is a white residue not soluble in ammonium hydroxid, lead has not been completely removed, or some substance not belonging to the group has been precipitated.

5. Neutralize the filtrate of 4 with nitric acid or boil off the ammonium hydroxid, and a white precipitate of silver chlorid proves the presence of silver. If the quantity of silver chlorid present is very small, it may be reduced by the mercury and escape solution in operation 4. In this case it will appear as a cloud in the solution of the next paragraph.

6. The blackening of the residue in operation 4 and its insolubility in ammonium hydroxid are proofs of the presence of mercury. Dissolve in a little aqua regia, nearly neutralize with ammonium hydroxid and add a strip of bright copper. A white deposit on the copper confirms mercury.

Notes.—*a.* Mercurous chlorid is soluble in ammonium chlorid and in alkali chlorids. If the solution should contain much of either of these, the mercury may not be precipitated. It will then be found in Group 2.

b. The student should know at all times just what reactions are taking place and should be able to write the equations in the usual way and also by ions. The equations for the principal reactions in the operations above are here given. Let the student work out similar equations for all his operations.

1. (a) $Ag^{+} + Cl^{-} \rightleftharpoons AgCl$ (b) $Hg_2^{++} + 2Cl^{-} \rightleftharpoons Hg_2Cl_2$
   (c) $Pb^{++} + 2Cl^{-} \rightleftharpoons PbCl_2$.
2. $PbCl_2 \rightleftharpoons Pb^{++} + 2Cl^{-}$.
3. (a) $Pb^{++} + CrO_4^{--} \rightleftharpoons PbCrO_4$ (b) $Pb^{++} + SO_4^{--} \rightleftharpoons PbSO_4$.
4. $AgCl + 2NH_4OH \rightleftharpoons Ag(NH_3)_2^{+} + Cl^{-} + H_2O$.
   $Hg_2Cl_2 + NH_4OH \rightleftharpoons Hg_2NH_2Cl + H^{+} + Cl^{-} + H_2O$.
5. $Ag(NH_3)_2^{+}, Cl^{-} + 2H^{+}, NO_3^{-} \rightleftharpoons AgCl + 2NH_4^{+}, NO_3^{-}$.
6. $Hg_2^{++} + Cu \rightleftharpoons 2Hg + Cu^{++}$.

TABLE FOR GROUP 1. BASIC ANALYSIS

Metals: Silver, mercurous mercury, lead.

Ions: Ag^+, Hg_2^{++}, Pb^{++}.

Group reagent: Dilute hydrochloric acid (chlorid ion).

Prepare solution, add reagent as directed, filter, wash.

Filtrate contains ions of Groups 2 to 6 with hydrogen ion and chlorid ion.

Precipitate AgCl, Hg_2Cl_2, $PbCl_2$. Treat on filter with hot water.

Solution contains $PbCl_2$. Cool. Crystals of $PbCl_2$. Divide the solution. a. Add K_2CrO_4. Yellow $PbCrO_4$ confirms **lead.** b. Add H_2SO_4. White $PbSO_4$ confirms **lead.**	Residue on filter AgCl, Hg_2Cl_2. Add dilute NH_4OH, collect filtrate.	
	Filtrate contains $Ag(NH_3)_2Cl$. Add HNO_3. White AgCl confirms **silver.**	Residue Hg_2NH_4Cl black. Dissolve in aqua regia, nearly neutralize with NH_4OH and add copper. White coating confirms **mercury.**

STUDENT'S NOTES

The student should keep in his note book a neat and complete record of his work according to the scheme below. The book should have an ample page so that the notes will not be crowded. The record may well extend across two pages.

PROBLEM I. BEGUN OCTOBER 1, 1910. SUPPOSED TO CONTAIN METALS OF GROUP 1

Operation	Material	Reagent	Result	Conclusion
1	Orig. solution	HCl	White precipitate	Group 1 present
2	Prec. from 1	Hot water	Residue	Ag or Hg
3	Filt. from 2	K_2CrO_4	Yellow prec.	*Pb present*
4	Prec. from 2	NH_4HO	Blackens	*Hg present*
5	Filt. from 4	HNO_3	White prec.	*Ag present*
5	Resid. from 4	Aq. reg., Cu.	White coat.	*Hg present*

Chapter VII

GROUP 2. COPPER-ARSENIC GROUP

Division A. Mercuric Mercury, Lead, Bismuth, Copper, Cadmium.
Division B. Arsenic, Antimony, Tin.

Properties and Reactions of the Metals and Ions of Group 2A

MERCURY

Metallic Mercury.—This has been described under Group 1.

Mercuric Compounds.—See mercurous compounds.

Mercuric Ion.—The mercuric ion, Hg^{++}, is colorless, bivalent, positive, quite active and poisonous. It may be identified by any of the reactions given below. The usual final test is the displacement of mercury by copper.

Mercuric Reactions.—Use 0.05 N. solution of mercuric chlorid, $HgCl_2$, equivalent 135.5. Dissolve 6.8 grams in one liter of water.

*1. **Hydrogen sulfid** precipitates black mercuric sulfiid, HgS, insoluble in dilute and in cold concentrated acids, in ammonium hydroxid and in ammonium sulfid; soluble in aqua regia, in alkali sulfids and in thiosalts generally. On first addition of the hydrogen sufid white $HgCl_2,2HgS$ is formed if the chlorid is used. As the reagent continues to act this turns orange, then brown and finally black as it is gradually decomposed and converted into HgS. This precipitate may be mistaken for antimony sulfid, from which it is easily distinguished by its insolubility in ammonium sulfid. Mercuric sulfid otherwise prepared is red and is the commercial substance known as vermilion. Its solubility in water is about 0.000012 gram to the liter. Mercuric sulfid dissolves in strong alkali solution of alkali sulfid, forming a thiosalt which yields the thiomercurate ion, HgS_2^{--}. On dilution with water the sulfid is reprecipitated.

$$HgS_2^{--} + H_2O = HgS + HS^- + HO^-.$$

2. **Ammonium sulfid** precipitates black mercuric sulfid at once.

*3. **Alkali hydroxids** give first a brown precipitate of mercuric hydroxid, $Hg(HO)_2$, which immediately changes to yellow mercuric oxid, HgO, soluble in acids even acetic, insoluble in alkalis, converted by ammonium hydroxid into the mercuric ammonium salt as shown in the next paragraph. It dissolves in water at 20° 0.05 gram to the liter.

*4. **Ammonium hydroxid** gives a white precipitate of the mercuric ammonium salt, the composition of which varies with the anion present, the chlorid and nitrate yielding respectively the compounds $HgNH_2Cl$ and $Hg_2ONH_2NO_3$. These salts are soluble in most acids, insoluble in alkalis.

5. **Ammonium carbonate** gives finally the same result as ammonium hydroxid.

6. **Alkali carbonates** precipitate reddish brown mercuric carbonate, $HgCO_3$, more or less basic, easily soluble in acids, decomposed by boiling into HgO and CO_2, by alkali hydroxids with separation of HgO, and by NH_4OH with precipitate as in 4.

*7. **Potassium iodid** precipitates mercuric iodid, HgI_2, soluble in acids and in alkalis. This compound is dimorphous, forming red quadratic and yellow rhombic crystals. It dissolves in excess of potassium iodid, yielding the complex ion, HgI_4^{--}, whose compound with potassium is K_2HgI_4, or K — I = I — Hg — I = I — K. It is a halosalt to which the name potassium iodomercurate may be applied. It is found in Nessler's solution. One liter of water dissolves about 0.05 gram HgI_2.

*8. **Stannous chlorid** reduces mercuric salts to mercurous chlorid which, being insoluble, separates, as a white precipitate,

$$2HgCl_2 + SnCl_2 \rightleftharpoons Hg_2Cl_2 + SnCl_4.$$

When the mixture is gently warmed with excess of the reagent, the mercurous chlorid is reduced and gray mercury separates,

$$Hg_2Cl_2 + SnCl_2 \rightleftharpoons 2Hg + SnCl_4.$$

*9. **Copper, zinc** and **iron** displace mercury.

10. **Dry reactions** are the same as for mercurous mercury.

LEAD

The properties and reactions of lead have been given under Group 1. If lead is present, it will always be found in Group 2, because of the solubility of its chlorid. It may not be found in Group 1 if the quantity present is small.

BISMUTH

Metallic Bismuth.—Bismuth is a brittle, pinkish white solid with metallic luster and specific gravity 9.8. It melts at 270°, boils at about 1,600°, and burns in the air to Bi_2O_3. It crystallizes in obtuse rhombohedrons which tarnish in moist air, becoming iridescent. It is insoluble in water and in cold hydrochloric and sulfuric acids. It dissolves in nitric acid to $Bi(NO_3)_3$ and in hot sulfuric acid to basic bismuthyl sulfate, $(BiO)_2SO_4$. It forms alloys with a number of metals, some of which melt at low temperatures and are called **fusible metals.**

Bismuth Compounds.—Bismuth is not chemically active and its compounds are not numerous. It is scarcely negative and its one or two acids are unstable. Its positive quality also is not strong, its hydroxid being a very weak base. It tends to form basic compounds containing the radicals BiO^+ and $Bi(HO)_2^+$.

Bismuth Ions.—None of the common salts of bismuth are soluble in water. The nitrate and chlorid are soluble in nitric and hydrochloric acids respectively. These solutions no doubt contain the bismuth ion, Bi^{+++}, which is colorless, trivalent and weakly basic. The radicals BiO^+ and $Bi(HO)_2^+$ can scarcely be regarded as ions, since they do not remain in solution.

Bismuth Reactions.—Use 0.03 N solution (better the bismuth nitrate (about 3 grams to the liter) in dilute nitric or hydrochloric acid just strong enough to hold the salt in solution. Make the solution first in the rather concentrated hot acid and add water. If a precipitate appears, add more acid or filter.

*1. **Water** added to a bismuth solution (better the bismuth solution added to water) causes precipitation because of the formation by hydrolysis of an insoluble bismuthyl compound.

$$Bi^{+++} + H_2O \rightleftharpoons BiO^+ + 2H^+.$$

The bismuthyl radical not being able to remain in solution as

an ion combines with the acid ion present. If the compound is the chlorid, the action is as follows:

$$Bi^{+++} + 3Cl^- + H_2O \rightleftharpoons BiOCl + 2H^+ + 2Cl^-.$$

Bismuthyl chlorid is scarcely soluble in the dilute acid and so the precipitation is practically complete. The nitrate gives at first the so-called sub-nitrate,

$$Bi(NO_3)_3 + H_2O \rightleftharpoons BiONO_3 + 2HNO_3, \text{ or}$$
$$Bi(NO_3)_3 + 2H_2O \rightleftharpoons Bi(HO)_2NO_3 + 2HNO_3.$$

Upon further addition of water the still more basic salt $O=Bi-O-Bi\begin{matrix}OH\\NO_3\end{matrix}$ is formed. The presence of sufficient acid prevents this precipitation. The precipitate dissolves on addition of acid and reappears on further dilution. This reaction is a good illustration of equilibrium and mass action.

*2. **Sulfid ion** (H_2S or $(NH_4)_2S$) precipitates bismuth sulfid, Bi_2S_3, dark brown, soluble in nitric and hydrochloric acid, insoluble in dilute acids, in ammonium sulfid and in alkali sulfids, the last distinguishing it from arsenic and antimony. No thiosalts of bismuth are known. One liter of water dissolves about 0.00018 gram of Bi_2S_3.

3. **Alkali hydroxids** precipitate in the cold white bismuth hydroxid, $Bi(HO)_3$, insoluble in excess, soluble in acids. On boiling the mixture the hydroxid loses water and becomes the metahydroxid $(BiO)OH$. On treating the alkalin liquid in which the hydroxid is suspended with chlorin, bromin, hypochlorites, or hydrogen peroxid, the precipitate turns brown, being oxidized to bismuthic acid.

$$(BiO)OH + 2NaHO + 2Cl = 2NaCl + H_2O + HBiO_2.$$

4. **Ammonium hydroxid** precipitates a white basic compound of varying composition, insoluble in excess of the reagent.

5. **Carbonate ions** (K_2CO_3, Na_2CO_3, $(NH_4)_2CO_3$) precipitate the basic carbonates, $(BiO)_2CO_3$ and $(BiH_2O_2)_2CO_3$, or carbonates still more basic, all insoluble in excess of the reagent soluble in acids, even acetic.

*6. **Potassium chromate** precipitates yellow basic bismuth chromate, $(BiO)_2CrO_4$, soluble in acids, insoluble in sodium hydroxid (difference from lead chromate), soluble in water about 0.0008 gram to the liter.

7. **Potassium dichromate** precipitates yellow bismuthyl dichromate, $(BiO)_2Cr_2O_7$, soluble in dilute nitric and hydrochloric acids, scarcely soluble in acetic acid, insoluble in alkali hydroxids (difference from lead). If the solution contains much acid, the precipitation is facilitated by addition of sodium acetate, the acetate ion removing the hydrogen ion by uniting to it to form undissociated acetic acid.

*8. **Alkali stannites** or alkalin solutions of stannous chlorid precipitate black metallic bismuth. The alkali first gives bismuth hydroxid and this oxidizes the stannite to stannate, being itself reduced to bismuth,

$$Bi^{+++} + 3HO^- = Bi(HO)_3,$$
$$2Bi(HO)_3 + 3SnO_2^{--} = 3SnO_3^{--} + 3H_2O + 2Bi.$$

If too much alkali is used, metallic tin separates; if too little, black stannous oxid may be thrown down.

The stannite solution is obtained by dissolving stannous chlorid in just enough alkali hydroxid to clear up the precipitate which is at first formed. It should be freshly prepared for each test since it quickly oxdizes to stannate.

9. **Chlorid ion** (KCl, NaCl) may not produce a precipitate since bismuth chlorid is soluble, but on dilution the oxychlorid is formed by hydrolysis as explained in 1 on page 66.

9a. **Potassium iodid** gives a dark red precipitate of bismuth iodid, BiI_3, soluble in excess to reddish yellow solution which contains the complex ion BiI_4^- the potassium compound of which probably has the structure $K - I = I - Bi = I_2$. On dilution bismuthyl iodid, BiOI, is formed by hydrolysis.

10. **Sulphuric acid** gives no precipitate. This and the chromate and dichromate reactions serve to distinguish bismuth from lead.

11. **Phosphate ions** precipitate white bismuth phosphate, $BiPO_4$,

soluble in concentrated acids except acetic, less soluble in dilute acids than most phosphates, insoluble in ammonium hydroxid.

12. **Zinc** displaces bismuth from its solutions.

13. **Dry Reactions.**—Bismuth compounds are reduced when heated with sodium carbonate on charcoal yielding a brittle metallic globule and a yellow coating of the oxid, Bi_2O_3.

COPPER

Metallic Copper.—Copper is a moderately hard malleable ductile metal of specific gravity 8.94. It has metallic luster and a peculiar copper-red color, melts at 1,057° and volatilizes in the electric arc. It tarnishes in moist air becoming coated with green basic copper carbonate and when heated oxidizes rapidly to cuprous and cupric oxids. It is rather low in the electrical potential series and is displaced by most metals. It is not readily acted upon by the acids because it is less positive than hydrogen and has no tendency to replace it. It decomposes hot sulfuric and hydrochloric acids giving with the former copper sulfate and sulfurous oxid and with the latter cuprous chlorid and hydrogen. It is a good conductor of electricity and forms several alloys of commercial importance.

Copper Compounds.—Copper forms cuprous and cupric compounds, but the former are unstable and are easily oxidized to the latter. Bivalent copper forms salts with the acids generally, while the principal cuprous salts are the halids and cyanids. In cuprous compounds, the copper is regarded as pseudo-monad, the double atom having a valence two, —Cu—Cu—. Because of copper's weak electric quality its salts hydrolyze yielding basic salts.

Copper Ions.—Of the copper compounds the nitrate, sulfate and chlorid dissolve readily in water yielding the copper ion, Cu^{++}, which has a blue color. Cuprous compounds are insoluble in water. Cuprous salts dissolve in the corresponding acids, but the cuprous ion, Cu_2^{++}, does not seem to separate and there is reason to believe that complex ions are formed. The blue copper ammonia ion, $Cu(NH_3)_4^{++}$, is formed when copper salts are dissolved in ammonium hydroxid.

Copper Reactions.—A. **Cupric ions.**—Use a 0.1 N solution of copper nitrate, $Cu(NO_3)_2$, $6H_2O$, equivalent 147.8; or of copper chlorid, $CuCl_2$, $2H_2O$, equivalent 85.2; or of copper sulfate, $CuSO_4$, $5H_2O$, equivalent 124.8. The sulfate solution should contain a little free sulfuric acid.

*1. **Sulfid ions** (H_2S or $(NH_4)_2S$) give a black precipitate of copper sulfid, CuS, insoluble in dilute acids, soluble in concentrated nitric acid, in hot hydrochloric acid, in potassium cyanid and in thiosulfates. Copper sulfid is slightly soluble in ammonium sulfid and hence may be found in Group 2 B. Its solubility in water is less than 0.000001 gram to the liter.

*2. **Alkali hydroxids** (NaHO or KHO) precipitate blue copper hydroxid, $Cu(HO)_2$, insoluble in excess, soluble in acids, in ammonium hydroxid, in ammonium salts and in alkali tartrates (Fehling's solution). When the suspended precipitate is warmed, it darkens losing water to become basic hydroxid, $(CuHO)_2O$, or copper oxid, CuO.

*3. **Ammonium hydroxid,** added drop by drop, throws down a green basic salt which dissolves even in slight excess to a soluble cupric ammonia compound,

$$2CuSO_4 + 2NH_4HO = (NH_4)_2SO_4 + (CuHO)_2SO_4$$
$$(CuHO)_2SO_4 + (NH_4)_2SO_4 + 6NH_4HO = Cu(NH_3)_4SO_4 + 8H_2O.$$

The solution contains the blue cupric ammonia ion, $Cu(NH)_4{}^{++}$. If alcohol is added, $Cu(NH_3)_4SO_4,H_2O$ separates. This ion is decomposed by H_2S, but is converted by KCN into the colorless cuprocyanid ion which is not affected by H_2S. See 5 below.

Ammonium carbonate gives the same reactions.

Alkali carbonates (Na_2CO_3 and K_2CO_3) precipitate green basic carbonate, $(CuHO)_2CO_3$, (native mineral malachite), insoluble in slight excess, dissolving to a blue solution in the strong reagent, readily soluble in acids and in ammonium hydroxid.

*5. **Potassium cyanid** precipitates green copper cyanid,

$Cu(CN)_2$, which immediately decomposes into cuprous cyanid and cyanogen,

$$2Cu(CN)_2 = Cu_2(CN)_2 + C_2N_2.$$

Cuprous cyanid dissolves in excess of the reagent forming the complex cuprocyanid ion, $Cu_2(CN)_4^{--}$, the structure of the potassium salt of which may be written,

$$\begin{array}{ccccccc} K-C=N & & & & & & N=C-K \\ \quad | \quad | & & & & & & \quad | \quad | \\ N=C-Cu-Cu-C=N & & & & & & \end{array}.$$

This ion is not decomposed by the sulfid ion. Cuprous cyanid is soluble in acids, in ammonium hydroxid and in ammonium salts.

6. **Potassium ferrocyanid** precipitates reddish brown cupric ferrocyanid, $Cu_2Fe(CN)_6$, insoluble in dilute acids, soluble in concentrated acids, decomposed by alkalis with separation of the hydroxid. It dissolves in ammonium hydroxid with formation of the blue copper ammonia ion.

7. **Potassium ferrocyanid** percipitates drab colored cupric ferricyanid, $Cu_3(FeC_6N_6)_2$, scarcely soluble in acids, soluble in ammonium hydroxid, decomposed by alkalis.

8. **Potassium iodid** reduces the cupric ion and precipitates cuprous iodid, $2Cu^{++} + 4I^- = Cu_2I_2 + I_2$. The liberated iodin colors the solution reddish brown and hides the color of the cuprous iodid. The precipitate may be separated by filtration or the color may be discharged by previously adding something which will reduce the iodin to iodid ion, such as ferrous sulfate or sodium sulfite.

9. **Potassium thiocyanate** gives a dark coloration or precipitate of cupric thiocyanate, $Cu(CNS)_2$, which slowly changes to white cuprous thiocyanate, $Cu_2(CNS)_2$. In the presence of a reducing agent (ferrous sulfate or sodium sulfite) the latter precipitate is formed at once. The reaction is as follows:

$$2Cu^{++} + 4CNS^- + SO_3^{--} + H_2O = Cu_2(CNS)_2 + SO_4^{--} + 2H^+ + 2CNS^-.$$

*10. **Reducing agents** convert cupric into cuprous compounds.

Copper sulfate is reduced in hot alkalin solution of glucose to red cuprous oxid, Cu_2O. This is the characteristic test for sugar.

11. **Zinc** and **iron** displace copper from its solutions.

12. **Dry Reactions.**—Copper compounds are reduced to metallic copper with sodium carbonate on charcoal in the reducing flame. Moistened with hydrochloric acid and introduced into the Bunsen flame on platinum wire they give the flame a blue or green color.

B. **Cuprous Ions.**—In the course of the analysis the cuprous ion will be oxidized to cupric ion and its reactions are only indirectly useful. Cuprous chlorid may be prepared as follows: Dissolve 3 grams $CuCl_2$ in 5 cc. water, add 3 cc. hydrochloric acid, introduce a strip of copper and boil for a few minutes. Remove the copper and add 2.5 cc. water. Set the white precipitate of Cu_2Cl_2 settle and wash once or twice by decantation. Keep the precipitate covered with water and use small portions dissolved in hydrochloric acid for the reactions.

1. **Alkali hydroxids** produce yellow cuprous hydroxid, $Cu_2(HO)_2$, which is converted by heat into cuprous oxid, Cu_2O. Both oxid and hydroxid dissolve in sulfuric acid with separation of metallic copper and oxidation to cupric sulfate.

$$Cu_2O + H_2SO_4 = Cu + CuSO_4 + H_2O.$$

Carbonate ions act in the same way as hydroxid ion since there is no cuprous carbonate.

2. **Sulfid ion** forms black cuprous sulfid, Cu_2S, soluble in warm dilute nitric acid with separation of sulfur.

3. **Potassium cyanid** precipitates white cuprous cyanid, $Cu_2(CN)_2$, soluble in excess with formation of the cuprocyanid ion, $Cu_2(CN)_4^{--}$, as in the case of cupric compounds.

4. **Ammonium hydroxid** makes a colorless solution of cuprous ammonia ion, $Cu_2(NH_3)_4^{++}$, which immediately turns blue by oxidation to cupric ammonia ion, $Cu(NH_3)_4^{++}$.

CADMIUM

Metallic Cadmium.—Cadmium is a white, malleable, ductile metal, a little heavier than tin, specific gravity 8.6. It melts at 320° and boils at 770° yielding a yellow vapor to disagreeable

odor. It tarnishes very slightly in the air and burns to CdO. It dissolves in dilute acids, evolving hydrogen, and with strong nitric acid acts like zinc.

Cadmium Compounds.—Cadmium is bivalent and wholly basic and its salts do not hydrolize with water. It unites with the negative elements generally and forms salts with most of the acids. Soluble compounds, are the chlorid, bromid, nitrate, sulfate and acetate.

Cadmium Ions.—Cadmium forms one well-defined elemental ion, Cd^{++}, colorless, bivalent, positive, wholly basic and poisonous. It forms with ammonium hydroxid the complex kation, $Cd(NH_3)_4^{++}$, and with cyanids the complex anion, $Cd(CN)_4^{--}$, both of which are decomposed by hydrogen sulfid.

Cadmium Reactions.—Use 0.1 N solution of the nitrate, $Cd(NO_3)_2$, $4H_2O$, equivalent 154.2; or chlorid, $CdCl_2$, $2H_2O$, equivalent 109.6; or sulfate $3CdSO_4$, $8H_2O$, equivalent 128.3.

*1. **Hydrogen sulfid** precipitates from neutral, alkalin or slightly acid cadmium solutions yellow cadmium sulfid, CdS, insoluble in alkali sulfids, (difference from arsenic, antimony and tin), in ammonium hydroxid, in alkali cyanids and in ammonium sulfid, soluble in HCl, in HNO_3 and in hot H_2SO_4. The complex cadmium ammonia and cadmium cyanid ions are decomposed by this reagent and the cadmium precipitated as sulfid. Hydrogen sulfid produces in solutions of cadmium halids an orange-yellow precipitate, the color of which grows lighter as the reagent continues to act. The final result is probably this:

$$Cd^{++} + H_2S \rightleftharpoons CdS + 2H^+.$$

This reaction is reversible, an excess of acid dissolving the sulfid. Precipitation is nearly complete in 0.5 N HCl solution. Cadmium sulfid dissolves in water 0.0013 gram to the liter.

2. **Ammoium sulfid** precipitates colloidal cadmium sulfid, which passes through the filter. The precipitation is completed by boiling or by the presence of salts.

3. **Alkali hydroxids** precipitate white amorphous cadmium hydroxid, $Cd(HO)_2$, insoluble in excess, soluble in ammonium hy-

droxid, in alkali cyanids and in acids. The ammonia and cyanid solutions contain the complex ions $Cd(NH_4)_4^{++}$ and $Cd(CN)_4^{--}$. One liter of water dissolves at 25° 0.0026 gram of $Cd(HO)_2$.

*4. **Ammonium hydroxid** precipitates cadmium hydroxid, which dissolves in considerable excess of the reagent with formation of the cadmium ammonia ion. The hydroxid is reprecipitated by dilution and heat.

5. **Carbonate ions** (Na_2CO_3,K_2CO_3, $(NH_4)_2CO_3$) give a white precipitate of basic cadmium carbonate of varying composition, insoluble in excess, but soluble in concentrated alkali carbonates and in acids. Ammonium hydroxid prevents the precipitation.

*6. **Potassium cyanid** precipitates white amorphous cadmium cyanid, $Cd(CN)_2$, which dissolves in considerable excess with formation of the complex cadmium cyanid anion,

$Cd^{++} + 2CN^- \rightleftharpoons Cd(CN)_2$, $Cd(CN)_2 + 2CN^- \rightleftharpoons Cd(CN)_4^{--}$.

From this solution the alkali hydroxids and carbonates do not precipitate the cadmium, but hydrogen sulfid decomposes the complex compound, throwing down cadmium sulfid. This action distinguishes cadmium from copper. Cadmium cyanid is soluble in acids and in ammonium hydroxid and water dissolves about 17 grams to the liter.

7. **Ferrocyanid ion** precipitates white cadmium ferrocyanid $Cd_2Fe(CN)_6$, insoluble in dilute acids, soluble in HCl and in NH_4OH, scarcely soluble in HNO_3 and in H_2SO_4.

8. **Ferricyanid ion** precipitates yellow cadmium ferricyanid, $Cd_3(FeC_6N_6)_2$, solubility like that of the ferrocyanid.

9. **Zinc** displaces cadmium from its solution.

10. **Dry Reactions.**—Cadmium compounds are easily reduced with alkali carbonates on charcoal, but the cadmium being volatile rises in the flame and is oxidized, producing a brown incrustation on the coal.

Properties and Reactions of the Metals and Ions of Group 2B

ARSENIC

Metallic Arsenic.—Arsenic is a brittle, steel-gray solid of

specific gravity 5.7. It crystallizes in rhombohedrons, melts only under pressure, sublimes when heated, yielding a yellow, poisonous vapor of disagreeable, garlic-like odor. It burns in the air to arsenous oxid, As_2O_3, and unites directly to most of the negative elements. It is insoluble in hydrochloric acid, but dissolves in nitric acid and in aqua regia, oxidizing to arsenous and arsenic acids.

Compounds of Arsenic—Arsenic acts with valences three and five, and its hydroxids are both acidic and basic. It is weakly basic and does not usually form salts with the oxyacids. Only the halids and the alkali arsenites and arsenates are soluble in water.

Ions of Arsenic.—Arsenic forms two positive elemental ions, arsenous ion, As^{+++}, and arsenic ion, As^{+++++}, the latter scarcely existing free, and also several oxyanions and thioanions, the most important of which are arsenite ion, AsO_3^{---}, arsenate ion, AsO_4^{---}, thioarsenite ion, AsS_3^{---}, and thioarsenate ion, AsS_4^{---}.

Arsenic is rather acidic than basic in its chemical relations. It yields, however, to the reducing action of hydrochloric acid and hydrogen sulfid, so that it appears with the sulfids of this group, mainly as arsenous sulfid, As_2S_3.

The double electric character of arsenic is shown by the reaction of arsenous oxid with certain reagents. This compound is slightly soluble in water with formation of arsenous hydroxid, which is very slightly ionized. The ionization takes place in two ways as follows:

$$As(HO)_3 = As^{+++} + 3HO^-, \quad (1)$$
$$As(HO)_3 = AsO_3^{---} + 3H^+. \quad (2)$$

The ionization is influenced by the presence of other ions according to law of mass action. If an acid be added, the concentration of the hydroxid ion is diminished, the dissociation goes according to (1) and the prevailing ion is As^{+++}. If an alkali be added, the concentration of the hydrogen ion is diminished and the ionization is increased according to (2). Hydrogen sul-

fid precipitates arsenous slufid from the acid solution, while, on the other hand, in the presence of the alkali, the thioarsenite anion is formed and remains dissolved:

$$2As^{+++} + 3H_2S = As_2S_3 + 6H^+,$$
$$AsO_3^{---} + 3H_2S = AsS_3^{---} + 3H_2O.$$

Arsenous Reactions.—Use 0.1 N hydrochloric acid solution of arsenous oxid, As_2O_3, equivalent 33. Dissolve 3.3 grams in hot hydrochloric acid and make up to one liter. Or dissolve 4.3 grams $NaAsO_2$ in one liter of water and acidify with HCl.

*1. **Hydrogen sulfid** precipitates from cold, better from hot acid arsenous or arsenite solutions yellow arsenous sulfid, As_2S_3, insoluble in dilute acids. Strong nitric acid oxidizes the arsenous sulfid to arsenic and sulfuric acids,

$$3As_2S_3 + 28HNO_3 + 4H_2O = 9H_2SO_4 + 28NO + 6H_3AsO_4.$$

Arsenous sulfid dissolves in hydroxids, carbonates and sulfids of alkalis and of ammonium to form thiosalts,

$$As_2S_3 + 6NH_4HO \rightleftharpoons (NH_4)_3AsO_3 + (NH_4)_3AsS_3 + 3H_2O,$$
$$As_2S_3 + 3Na_2CO_3 = Na_3AsS_3 + Na_3AsO_3 + 3CO_2,$$
$$As_2S_3 + 3(NH_4)_2S \rightleftharpoons 2(NH_4)_3AsS_3.$$

If a polysulfid is present, thioarsenite is oxidized to thioarsenate.

Acids decompose these compounds and reprecipitate the sulfid,

$$2AsS_3^{---} + 6H \rightleftharpoons As_2S_3 + 3H_2S.$$

One liter of water dissolves about 0.0005 gram As_2S_3 and the compound undergoes slow decomposition as follows:

$$As_2S_3 + 3H_2O = As_2O_3 + 3H_2S.$$

2. **Ammonium sulfid** slowly added precipitates at once and almost completely arsenous sulfid soluble in excess to thioarsenite.

*3. **Fehling's solution** oxidizes in neutral or alkaline solution arsenous to arsenic ion with separation of cuprous oxid,

$$As^{+++} + 2Cu^{++} + 2HO^- = As^{+++++} + Cu_2O + H_2O.$$

The mixture must be warmed but not boiled. This reaction serves to identify arsenous ion in presence of arsenic ion.

*4. **Copper** displaces arsenic in all its forms. If a strip of copper is introduced into the solution made acid with HCl and the mixture warmed, the arsenic is deposited on the copper.

*5. **Dry Reactions.**—*a*. When arsenic is heated on charcoal, it burns with characteristic garlic-like odor. The odor must be taken cautiously, as the oxid is quite poisonous.

b. Arsenic compounds are easily reduced with carbon in a closed tube, the arsenic forming a sublimate on the tube.

Arsenic Reactions.—The compounds which contain pentavalent arsenic behave very much like the arsenous compounds. They are rather easily reduced by hydrogen sulfid and sulfurous oxid, and will, in the course of the analysis, appear mainly as arsenous compounds. The arsenates of potassium, sodium and ammonium are soluble in water.

Use 0.05 N solution of potassium or sodium arsenate, K_2HAsO_4, equivalent 73. A solution of arsenic acid may be made as follows: Boil about 3 grams of As_2O_5 in strong nitric acid till red fumes cease to come off, then dilute to one liter.

*1. **Hydrogen sulfid** in neutral or alkalin solutions produces no precipitate since the soluble thioarsenate is formed,

$$K_3AsO_4 + 4H_2S = K_3AsS_4 + 4H_2O.$$

The addition of hydrochloric acid throws down the yellow arsenic sulfid slowly and best on boiling,

$$2K_3AsS_4 + 6HCl = 6KCl + 3H_2S + As_2S_5,$$

or by ions,

$$2AsS_4^{---} + 6H^+ = As_2S_5 + 3H_2S.$$

In acid solutions hydrogen sulfid precipitates a mixture of As_2S_5, As_2S_3 and S because of the reducing action of the acid and the reagent. If the solution is strongly acid, the precipitate is mainly As_2S_5 and falls promptly; if it is weakly acid, below 2 normal As_2S_3 prevails and the precipitation is quite slow. Heat favors the precipitation. The reduction may be hastened by the use of a more powerful agent such as sulfurous oxid. Arsenic sulfid is insoluble in dilute acids but dissolves in alkali and ammonium sulfids and carbonates to thioarsenates. The reactions are similar to those given under arsenous sulfid.

2. **Ammonium sulfid** added slowly to the acid solution precipitates at once and almost completely arsenic sulfid, As_2S_5, soluble in excess of the reagent to thioarsenate.

3. **Potassium iodid** with **hydrochloric acid** reduces quinquevalent arsenic with liberation of iodin which colors the solution red, or blue if K I-starch has been added. It must be remembered that other things set iodin free such as chromate, dichromate and nitrite ions.

4. **Magnesia mixture** gives with ammoniacal arsenate solutions a white crystallin precipitate of magnesium ammonium arsenate, $Mg\ NH_4\ PO_4$, soluble in acids.

Special Tests for Arsenic.—*1. *Marsh's Test.* In the presence of nascent hydrogen compounds of arsenic are reduced and hydrogen arsenid, H_3As, is formed, a compound which is readily decomposed by heat with deposition of metallic arsenic. This constitutes Marsh's test for arsenic.

Zinc and sulfuric acid are used as the source of the nascent hydrogen. To an evolution bottle containing some arsenic-free zinc dilute sulfuric acid (sp. gr. 1.2) is added until the hydrogen is coming off rather freely. The bottle is furnished with a horizontal delivery tube drawn to a point. When the air has been expelled, the jet of gas is lighted and a cold plate is held in the flame. If no spot is produced on the plate, arsenic is absent. Add to the bottle through the funnel tube a few drops of the solution to be tested. Watch the flame for change of color and character and let it play again upon the plate. If arsenic is present, it will be reduced by the hydrogen, will be converted into hydrogen arsenid, and passing out will burn with the hydrogen at the jet. Its presence will be shown in three ways:

a. The flame will become gray or whitish because of the formation of arsenous oxid; As_2O_3. If much arsenic is present white fumes will appear.

b. When a cold porcelain plate (evaporating dish or crucible lid) is held in the flame, the arsenic cooled below its burning temperature will be deposited on the plate as a black spot with metallic luster. The spot is soluble in sodium hypochlorite (difference from antimony).

c. If the delivery tube be heated, a ring of metallic arsenic will be deposited on the tube beyond the heated point.

Antimony compounds give similar results, but the spot is devoid of metallic luster and is insoluble in sodium hypochlorite.

2. *Reinsch's Test for Arsenic.*—If a strip of polished copper is added to a hydrochloric acid solution of arsenous oxid or of an arsenite and the mixture warmed, the arsenic is deposited on the copper, uniting with it to form a gray coating of copper arsenid, Cu_3As_2. If the copper be dried and heated in a dry test-tube the arsenic sublimes and is partly oxidized to arsenous oxid, As_2O_3, which is deposited in octohedral crystals on the tube.

This test cannot be relied on without confirmation since mercury, silver, gold, platinum, some sulfur compounds and some organic substances produce similar stains on copper.

3. *Bettendorf's Test for Arsenic.*—Stannous chlorid in strong hydrochloric acid solution reduces compounds of arsenic. Mix the solution to be tested with an equal volume of strong hydrochloric acid and add a saturated hydrochloric acid solution of tin chlorid. The arsenic separates as a dark brown powder.

4. *Fleitmann's Test.*—When an arsenous solution is warmed in a test-tube with sodium hydroxid and metallic zinc, hydrogen arsenid is evolved and blackens (precipitated silver) paper moistened with silver nitrate and held at the mouth of the tube. Hydrogen antimonid is not produced when antimony compounds are treated in the same way.

ANTIMONY

Metallic Antimony.—Antimony is a silver-white, brittle, solid with metallic luster, and specific gravity 6.7 to 6.8. It crystallizes in rhombohedrons, melts at 630° and distills at 1,450°. It unites directly with the halogens and burns in the air to antimonous oxid, Sb_2O_3. It is insoluble in water and in dilute acids, dissolves in strong hydrochloric and sulfuric acids to form the chlorid and sulfate, and is oxidized by nitric acid to the oxids, Sb_2O_3 and Sb_2O_5, which are very slightly soluble in the strong acid. It is a constituent of several alloys such as type-metal and Babbitt-metal.

Antimony Compounds.—Antimony forms compounds similar to those of arsenic. Its hydroixds are both acidic and basic and its salts hydrolize with formation of difficulty soluble oxy-compounds.

Ions of Antimony.—Antimony forms two elemental ions, antimonous Sb^{+++}, and antimonic Sb^{+++++}, the latter not very well defined and easily reduced to the former. There is also a basic antimonyl ion, SbO^{+}, which is formed by hydrolysis when an antimonous solution is diluted,

$$SbCl_3 + H_2O = 2HCl + SbOCl.$$

On adding more water or boiling the mixture the oxid is thrown down,

$$2SbCl_3 + 3H_2O = 6HCl + Sb_2O_3.$$

The anions of antimony will be treated under acidic analysis. Antimony forms thioanions similar to those of arsenic.

Antimonous Reactions.—In the course of the analysis antimonic compounds are mostly reduced and it will be antimonous reactions with which the student will generally meet.

Use a 0.02 N hydrochloric acid solution of antimonous chlorid, $SbCl_3$, equivalent 75. Dissolve 15 grams of $SbCl_3$ or 10 grams of Sb_2O_3 in concentrated hydrochloric acid and make up to one liter. If a precipitate forms on dilution, add acid enough to dissolve it or let it settle and decant or filter.

A solution of potassium antimonyl tartrate (tartar emetic), $KSbOC_4H_4O_6$, may be used. Dissolve 16 grams in dilute hydrochloric acid and dilute to one liter. The oxychlorid is soluble in tartaric acid and there may be no precipitate formed on dilution.

*1. **Dilution.**—On diluting the hydrochloric acid solution, best by pouring the solution into water, a white precipitate of antimonyl chlorid, SbOCl, is thrown down. This precipitate is distinguished from the similar bismuthyl chlorid by its dissolving in tartaric acid to antimonyl tartrate, $(SbO)_2C_4H_4O_6$. On boiling with water the antimonyl chlorid is converted into antimonous oxid. See under Ions of Antimony above.

*2. **Alkali hydroxids** and **carbonates** (HO^- and CO_3^{--} ions) precipitate white antimonous hydroxid, $Sb(HO)_3$. This compound is both acidic and basic, undergoing a two-fold dissociation as in the case of arsenous hydroxid. It, therefore, dissolves in the alkali hydroxids to form metantimonites and in acids to antimonous salts.

3. **Ammonium hydroxid** precipitates antimonous hydroxid insoluble or scarcely soluble in excess of the reagent.

*4. **Hydrogen sulfid** precipitates orange-red antimonous sulfid.

$$2SbCl_3 + 3H_2S \rightleftharpoons Sb_2S_3\ 6HCl.$$

If the solution is too strongly acid, the reaction reverses and the sulfid is redissolved; on the other hand if it is too dilute, antimonyl chlorid falls. It is best therefore to conduct the gas through the solution for a time and then dilute.

Antimonous sulfid dissolves in alkali hydroxids to metantimonites, in ammonium sulfid to unstable thioantimonites, in yellow ammonium sulfid to thioantimonates. From these solutions acids precipitate the sulfid. Antimonous sulfid is insoluble in ammonium carbonate, soluble in ammonium hydroxid, in concentrated acids and in sodium carbonate. Water dissolves 0.001 gram Sb_2S_3 to the liter.

5. **Ammonium sulfid** precipitates antimony sulfid which dissolves in excess with formation of thioantimonite ion, SbS_3^{---}.

*6. **Nascent hydrogen** reduces antimony compounds just as it does arsenic compounds with formation of hydrogen antimonid, H_3Sb, which, burned from a jet, against a cold plate, deposits metallic antimony. The operation is conducted as in Marsh's test for arsenic. The antimony spot is distinguished from the arsenic spot as follows:

a. It is blacker and less metallic in luster,

b. It does not dissolve in hypochlorite solution,

c. Hydrogen sulfid passed over the antimony stain in the tube colors it orange.

*7. **Zinc** displaces antimony from hydrochloric acid solutions by galvanic action. If a strip of zinc and a strip of platinum are

brought together in the solution, the antimony is deposited on the platinum as a black stain not soluble in the acid when the zinc is removed (difference from tin). Antimony is also displaced by iron and tin.

8. **Dry Reactions.**—Heated on charcoal with potassium carbonate and potassium cyanid, antimony compounds are reduced and a brilliant globule of the metal is obtained which burns in the flame to white antimonous oxid, Sb_2O_3.

Antimonic Reactions.—Use 0.05 N solution of antimonic chlorid $SbCl_5$, equivalent 59.5. Dissolve 3 grams in dilute hydrochloric acid and make up to one liter. If a precipitate forms on dilution, add acid until it dissolves.

A solution of antimonic oxid of sufficient concentration to show all the reactions except that of dilution may be obtained by boiling antimonic oxid, Sb_2O_5, in hydrochloric acid.

*1. **Dilution** precipitates antimonic oxychlorid, SbO_2Cl, at first and then on warming an antimonic acid, H_3SbO_4.

$$SbCl_5 + 2H_2O = 4HCl + SbO_2Cl.$$
$$SbO_2Cl + 2H_2O = HCl + H_3SbO_4.$$

Tartaric acid prevents the precipitation.

*2. **Hydrogen sulfid** precipitates slowly orange-red antimonic sulfid mixed with more or less of antimonous sulfid and sulfur because of the reducing action of the reagent. Antimonic sulfid dissolves in strong acids, in alkali hydroxids, and in alkali and ammonium sulfids. With alkali and ammonium sulfids it forms thiosalts and with alkali hydroxids thio and oxythio salts,

$$Sb_2S_5 + 3\ (NH_4)_2S = 2\ (NH_4)_3SbS_4,$$
$$Sb_2S_5 + 6KHO = K_3SbS_4 + K_3SbSO_3 + 3H_2O.$$

3. **Ammonium sulfid** precipitates antimonic sulfid which dissolves in excess with formation of thioantimonate ion, SbS_4^{---}.

4. **Alkali hydroxids** scarcely make a precipitate because of immediate formation of alkali antimonates.

5. **Ammonium hydroxid** precipitates antimonic acid scarcely soluble in excess.

6. **Nascent hydrogen** forms hydrogen antimonid just as with antimonous compounds.

7. **Potassium iodid** acts with antimony compounds just as it does with arsenic compounds.

TIN

Metallic Tin.—Tin is a silver-white, malleable, ductile metal with specific gravity 7.3, melting-point 235° and boiling-point 1,650°. It does not tarnish in pure air, but is darkened by hydrogen sulfid. It burns to stannic oxid, SnO_2, and dissolves in dilute acids to form stannous salts. Strong nitric acid converts it into metastannic acid, H_2SnO_3, which polymerizes to $(H_2SnO_3)\ x$ in which x is probably 5.

Tin Compounds.—Tin unites with many of the negative elements and forms salts with most of the acids. It also forms numerous alloys, among which may be mentioned solder, bronze, pewter and bell-metal. It exhibits valences two and four. Bivalent tin is usually basic while tetravalent tin is mostly acidic. All tin salts hydrolize more or less.

Tin Ions.—The basic ions of tin are stannous ion, Sn^{++}, and stannic ion, Sn^{++++}. The principal anions are stannite, SnO_2^{--}, stannate, SnO_3^{--}, and thiostannate, SnS_3^{--}. There are also halostannite and halostannate ions. Stannous ion is easily oxidized to stannic ion and also to stannate ion, and is therefore a reducing agent. The ions of tin are all colorless.

Stannous Reactions.—Use 0.05 N solution of stannous chlorid, $SnCl_2$. Dissolve 6 grams of tin foil in dilute hydrochloric acid, make up to one liter and add a few pieces of tin. If a precipitate forms on dilution, add more acid.

*1. **Hydrogen sulfid** precipitates brown stannous sulfid, SnS, soluble in strong, but not in dilute acids; soluble in yellow ammonium sulfid, not to thiostannite, but to thiostannate ion, from which acids precipitate stannic sulfid, SnS_2. Stannous sulfid is insoluble in ammonium carbonate and in colorless ammonium sulfid; it is oxidized by aqua regia to stannic chlorid, $SnCl_4$. It dissolves in water 0.00002 gram to the liter.

Ammonium sulfid gives the same precipitate as hydrogen sulfid, which dissolves in excess to thiostannite and thiostannate.

*2. **Alkali hydroxids** (KHO and NaHO) precipitate white stannous hydroxid, $Sn(HO)_2$, soluble in excess of the alkali and in acids. This shows that the hydroxid is both acidic and basic and that it dissociates in two ways,

$$(a)\ Sn(HO)_2 + 2H^+ = Sn^{++} + H_2O,$$
$$(b)\ Sn(HO)_2 + 2HO^- = SnO_2^{--} + 2H_2O.$$

The alkali stannite is unstable and on warming becomes stannate with separation of tin,

$$2SnO_2^{--} + H_2O = SnO_3^{--} + 2HO^- + Sn.$$

3. **Ammonium hydroxid** precipitates stannous hydroxid, only slightly soluble in excess.

4. **Alkali carbonates** precipitate stannous hydroxid, the carbonate, if it is formed, being hydrolized at once,

$$SnCO_3 + 2H_2O = Sn(HO)_2 + H_2O + CO_2.$$

The precipitate slowly dissolves, being transformed into stannite.

*5. **Oxidation** of stannous to stannic ion is effected in various ways among which are the following:

a. Mercuric chlorid oxidizes stannous to stannic chlorid, being itself reduced to mercurous chlorid or to mercury,

$$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4.$$
$$Hg_2Cl_2 + SnCl_2 = 2Hg + SnCl_4.$$

b. Ferric ion is reduced to ferrous ion with corresponding elevation of the valence of tin:

$$2Fe^{+++} + Sn^{++} = 2Fe^{++} + Sn^{++++}.$$

c. Gold chlorid effects the oxidation, being itself reduced to the metallic state,

$$2AuCl_3 + 3SnCl_2 = 3SnCl_4 + 2Au.$$

d. Copper and bismuth salts are reduced, giving stannic ion.

e. Chromates, arsenates, antimonates, and permanganates, and also nitric acid, oxidize stannous to stannic ion.

f. Bromin water oxidizes stannous ion becoming bromid ion.

*6. **Zinc** displaces tin from weakly acid stannous or stannic solutions and the tin is deposited on the zinc as a black spongy coating, soluble in the acid (difference from antimony). The test is made by adding a few drops of the solution to a piece of platinum foil and introducing a strip of zinc so that it comes in contact with the platinum. The tin is deposited on both the metals, but quickly dissolves from the platinum when the zinc is removed.

7. **Dry Reactions.**—When heated on charcoal with sodium carbonate and potassium cyanid all tin compounds are reduced to the metallic state and the coal is covered with a white incrustation of stannic oxid, SnO_2.

Stannic Reactions.—Stannic oxid is practically insoluble in water and in acids and the salts cannot be obtained directly. The soluble stannic salts generally hydrolize with separations of stannic hydroxid.

Use 0.05 normal hydrochlorid acid solution of stannic chlorid, $SnCl_4$, which may be conveniently obtained by oxidizing the stannous chlorid solution with bromin water, adding the latter until the brown color is no longer discharged, $Sn^{++} + Br_2 = Sn^{++++} + 2Br^-$, or by dissolving stannic chlorid in water acidulated with HCl.

*1. **Hydrogen sulfid** precipitates yellow stannic sulfid, SnS_2, insoluble in dilute acids, soluble in alkalis, alkali sulfids and carbonates, and in ammonium sulfid with formation of thiostannates,

$$3SnS_2 + 6KHO = 2K_2SnS_3 + K_2SnO_3 + 3H_2O,$$
$$3SnS_2 + 3Na_2CO_3 = 2Na_2SnS_3 + Na_2SnO_3 + 3CO_2;$$
$$SnS_2 + (NH_4)_2S = (NH_4)_2SnS_3.$$

From these solutions acids reprecipitate stannic sulfid. It dissolves in water 0.002 gram to the liter.

Ammonium sulfid gives the same precipitate soluble in excess.

*2. **Hydroxid ions** (KHO, NaHO and NH_4OH) throw down a white gelatinous precipitate of stannic acid which has the formula H_4SnO_4 when dried in the air and H_2SnO_3 when dried over sulfuric acid:

$$SnCl_4 + 4KHO = H_4SnO_4 + 4KCl.$$

The precipitate dissolves in excess to form meta salts:

$$H_4SnO_4 - 2KHO = K_2SnO_3 + 3H_2O.$$

This compound is called **alpha-stannic acid** to distinguish it from the acid described below and its salts are called **stannates** though they are really of the meta form.

Alpha-stannic acid is readily soluble in dilute acids to form stannic salts. In this relation it is basic and its name and formula should be stannic hydroxid, $Sn(HO)_4$. The stannic salts are unstable and the acid is reprecipitated on warming.

*3. **Nitric Acid.**—When tin is dissolved in strong nitric acid, or when nitric acid is added to stannic solutions, a white amorphous powder is obtained which has the empirical formula, H_4SnO_4, or when dried over sulfuric acid, H_2SnO_3; that is, it has the same composition as alpha-stannic acid. Its properties, however, are very different, and investigations have shown that its molecular formula is probably $H_{10}Sn_5O_{15}$, or $(H_2SnO_3)_5$. It is called **beta-stannic acid** or **meta-stannic acid.** Strong hydrochloric acid converts it into a complex compound called beta-stannic chlorid, or better stannyl chlorid, $Sn_5O_5Cl_2(HO)_8$, soluble in water but not in hydrochloric acid. Sulfate ion forms a similar beta-stannic sulfate.

4. **Alkali carbonates** precipitate stannic acids easily soluble in excess of potassium carbonate.

5. **Chlorids** react with stannic chlorid to form chlorstannates, an example of which is $(NH_4)_2SnCl_6$. The other halids act in the same way, while cyanid ion precipitates stannic hydroxid.

6. **Iron** reduces stannic to stannous ion but does not set the tin free (difference from antimony).

Analysis of the Copper-Arsenic Group

SEPARATION AND IDENTIFICATION OF THE METALS AND IONS OF GROUP 2

Metals, other than those of Group 1, whose sulfids are insoluble in dilute acids.

Division A. Copper Group.—Metals of Group 2 whose sulfids are insoluble in ammonium sulfid or sodium carbonate.

Metals: Mercuric mercury, lead, bismuth, copper, cadmium.

Ions: Hg^{++}, Pb^{++}, Bi^{+++}, Cu^{++}, Cd^{++}.

Division B. Arsenic Group.—Metals of Group 2 whose sulfids are soluble in ammonium sulfid and in sodium carbonate.

Metals: Arsenic, antimony, tin.

Ions: As^{+++}, As^{+++++}, Sb^{+++}, Sb^{+++++}, Sn^{++}, Sn^{++++}.

Group reagent: Hydrogen sulfid in presence of hydrochloric acid, or sulfid ion in presence of hydrogen ion.

Division reagent: Ammonium sulfid or sodium carbonate.

Several of the metals of this group, particularly those of Division B, form oxy-, thio- and halo-anions. For proper separation these ions must be decomposed and converted into kations. This change is effected through the reducing action of the group reagent and no special treatment is necessary.

Principle.—The ions of this group react with the sulfid ion to form sulfids which are insoluble in dilute acids. They will, therefore, be precipitated from acid solutions on addition of a soluble sulfid. The presence of the acid prevents the precipitation of the metals of Groups 3 and 4 whose sulfids are soluble in acids.

The Group Reagent.—Any soluble sulfid will serve as reagent for this group. Hydrogen sulfid is used because the hydrogen ion left in the solution does not interfere with the reactions which are to follow and because the excess of hydrogen sulfid can be easily expelled from the solution by boiling. Practically, hydrogen sulfid from the generator is allowed to bubble through the solution until it is saturated and until the precipitation is complete. The action is hastened by heat and some times by dilution. It will be found advantageous to use a small flask furnished with a stopper through which a tube passes connected with the generator. A slight pressure is thus obtained and by frequently shaking the closed flask the saturation and precipitation are soon complete.

The Precipitate.—The precipitate of this group is separated into two divisions, based upon its action with ammonium sulfid,

the first being insoluble and the second soluble in that reagent. The first division includes HgS black, PbS black, Bi_2S_3 brown, CuS black, CdS yellow. To the second division belong As_2S_3 yellow, As_2S_5 yellow, Sb_2S_3 orange-yellow, Sb_2S_5 orange-yellow, SnS brown, SnS_2 yellow. Arsenic and antimony may be present with valences three and five, and tin with valences two and four; hence the mixed precipitates.

The dissociation of hydrogen sulfid in contact with water is very slight, about 0.07 per cent. in decinormal solution. This small amount of the sulfid ion is sufficient to start the reaction and rapid dissociation of the hydrogen sulfid to maintain the value of the ionic product supplies more sulfid ions until the metal is all precipitated.

Letting M represent a metal of the group, the reactions may be written as follows:

$$M^{++} + S^{--} = MS, \qquad M^{++++} + 2S^{--} = MS_2,$$
$$2M^{+++} + 3S^{--} = M_2S_3, \qquad 2M^{+++++} + 5S^{--} = M_2S_5.$$

If we regard the action as taking place between the metallic ion and the undissociated hydrogen sulfid, we shall have the equations,

$$M^{++} + H_2S = MS + 2H^+,$$
$$M^{++++} + 2H_2S = MS_2 + 4H^+,$$
$$2M^{+++} + 3H_2S = M_2S_3 + 6H^+,$$
$$2M^{+++++} + 5H_2S = M_2S_5 + 10H^+.$$

Sometimes a finely divided yellow precipitate of sulfur separates on adding the hydrogen sulfid. This will always occur when oxidizing agents are present. Such precipitate need not be mistaken for the sulfids, since these are flocculent and settle quickly.

Division Reagent.—There are four reagents which may be used for the separation of the divisions of this group: ammonium sulfid, yellow ammonium sulfid, alkali sulfid, and sodium carbonate. The first dissolves all the sulfids of Division B, except stannous sulfid; the second dissolves them all, together with some copper; the third dissolves them all, together with mercury; the fourth dissolves all, but rather slowly, and only in concentrated solution. In the course of the analysis stannous is easily oxidized to stannic ion by addition of a few drops of nitric acid, and then

amomnium sulfid is the most convenient reagent. This is the author's method and has proved very satisfactory even in the hands of beginners.

The first three reagents dissolve the sulfids by converting them into thiosalts which dissociate yielding thioanions,

$$As_2S_3 + 3(NH_4)_2S \rightleftharpoons 2(NH_4)_3AsS_3 \rightleftharpoons 6NH_4^+ + 2AsS_3^{---}.$$

The sulfids are reprecipitated by hydrochloric acid thus:

$$2AsS_3^{---} + 6H^+ \rightleftharpoons As_2S_3 + 3H_2S.$$

Sodium carbonate gives both thio and oxysalts and sometimes oxythiosalts. The reactions are somewhat as follows:

$$As_2S_3 + 3Na_2CO_3 \rightleftharpoons Na_3AsS_3 + Na_3AsO_3 + 3CO_2,$$
$$Sb_2S_5 + 3Na_2CO_3 \rightleftharpoons Na_3SbS_4 + Na_3SbSO_3 + 3CO_2.$$

Preparation of the Solution.—Use the filtrate from Group 1. If Group 1 was absent, use the original solution acidified as directed in 1 below. If the acid produces a precipitate not belonging to the group, its nature will already have been ascertained. If oxidizing substances are present, they will be decomposed by the hydrogen sulfid with separation of much sulfur, and it is best to remove them before applying the reagent. This is mainly accomplished by the boiling with hydrochloric acid. If stronger oxidizers are present, such as nitric acid, nitrates and chlorates, the evaporation should be carried nearly to dryness and the residual liquid diluted with the proper quantity of water. In this case a notable quantity of arsenous ion may be lost.

A. Group Precipitation

For the ready precipitation of quinquevalent arsenic by hydrogen sulfid an HCl concentration above 2 N is required; for the complete precipitation of other members of the group, notibly cadmium, antimony and tin, the acid concentration should be below 0.5 N; to hold in solution the metals of the succeeeding groups the acid concentration must be above 0.1 N. These different concentrations are secured first by evaporation, then by dilution.

Arsenous chlorid in hydrochloric acid solution is volatil, but the quantity lost on boiling is a *function of the quantity present* and also of the acid concentration. When an arsenous solution normal in HCl is boiled half away, less than one thousandth of

the arsenic is lost. The increased concentration more than compensates for this loss. See Hinds in *Jr. of Am. Chem. Soc.* June, 1912.

1. To a given quantity of the solution (say 45 cc.) add one-ninth its volume (5 cc.) of concentrated hydrochloric acid and a few drops (0.5 cc.) of nitric acid. The laboratory hydrochloric acid is usually about 10 N and the solution is thus made about normal. If much acid is already present, allowance must be made for it. Transfer the mixture to an Erlenmeyer flask and boil it a little more than half way under the hood. The residual liquid is about 2 N in HCl, since but little acid is lost on boiling at this concentration. The nitric acid has oxidized stannous to stannic ion, his prevented separation of metals by reduction, and has probably raised the valence of a portion of the arsenic. If quinquevalent arsenic is known to be absent, add 3 cc. of HCl instead of 5 and boil for only a few minutes.

Pass a rapid stream of hydrogen sulfid through the hot liquid, heating again to boiling once or twice and shake vigorously. When no more precipitate forms, (5 to 10 minutes), add enough water (80 cc.) to make the volume a little more than twice the original (100 cc.), thus bringing the HCl concentration below 0.5 N. Continue to pass the gas until the liquid is cold and the precipitation complete (10 to 15 minutes). Filter, wash with water containing hydrogen sulfid and throw away the washings.

The filtrate contains the ions of Groups 3, 4, 5 and 6, together with hydrogen ion, partly resulting from the reaction, and chlorid ion introduced with the acid, besides any anion which may have been in the original solution. It should be freed at once from hydrogen sulfid by boiling, otherwise sulfate ion is formed by oxidation and may precipitate the ions of the calcium group.

The precipitate may be:

A. Hgs, Pbs, Bi_2S_3, CuS, CdS.
B. As_2S_3, As_2S_5, Sb_2S_3, Sb_2S_5, SnS_2.

B. Separation of Divisions A and B

2. (*a*) With Ammonium Sulfid.—Transfer a portion of the precipitate to a beaker, cover it with concentrated ammonium

hydroxyd, pass a rapid stream of hydrogen sulfid for one or two minutes, warm gently, shake well, filter and wash free from chlorids with water containing hydrogen sulfid. The sulfids of arsenic antimony and tin dissolve very promptly, carrying with them only a trace of copper.

If stannous ion has not been oxidized, the precipitate should be covered with yellow ammonium sulfid, warmed and filtered. In this case, some copper will dissolve and will interfere with the tests for antimony and tin. To affect its removal, make the solution (filtrate of 11 below) alkalin with potassium hydroxid, filter off the copper oxid, then make the filtrate acid with hydrochloric acid.

The residue consists of the sulfids of the metals of Group 2 A.

The filtrate contains the ammonium thiosalts of the metals of Group 2 B, of which the anions are AsS_3^{---}, AsS_4^{---}, SbS_3^{---}, SbS_4^{---}, SnS_2^{--}, SnS_3^{--}.

b. With Sodium Carbonate.—Treat the precipitate of 1 with 25 cc. 3 N Na_2CO_3, add 20 cc. 3 per cent. solution of H_2O_2, heat to 50°, dilute to 200 cc., pass a little H_2S to precipitate any copper that may have been oxidized, filter, wash.

The residue is the same as under 2 A. Continue as under 3.

The filtrate contains the thio- and oxyanions of Group 2 B. Continue as under 16 on page 95.

C. Separation of the Ions of Group 2A, Copper Group

3. Transfer a portion of the residue of 2 to a porcelain dish or to a beaker, add a little dilute nitric acid and warm. If hydrochloric acid is present, it must be removed, otherwise aqua regia will be formed, which dissolves HgS. The sulfids all dissolve except mercuric sulfid with evolution of hydrogen sulfid, which is partly oxidized to sulfur and sulfuric acid. Filter and wash with hot water, to which a drop of nitric acid has been added, rejecting the washings. The separated sulfur is colored dark by the sulfids, but is easily recognized, since it gathers together and floats.

The residue is black HgS or a mixture of HgS with white

$Hg(NO_3)_2,2HgS$. A white residue may be lead sulfate or stannic acid.

The filtrate contains the ions of lead, bismuth, copper, cadmium, Pb^{++}, Bi^{++}, Cu^{++}, Cd^{++}, along with nitrate ions.

4. Dissolve the residue of 3 in a small quantity of hot aqua regia, evaporate or neutralize excess of acid, add HCl, dilute, and filter if necessary. The mercuric sulfid goes into solution as mercuric chlorid.

a. Add to portion of the clear solution stannous chlorid. The mercuric ion is reduced and white mercurous chlorid, Hg_2Cl_2, or gray mercury is precipitated.

b. Neutralize another portion with NaOH, add HCl to acidity and add a strip of copper. White stain on the copper confirms mercury.

5. Add sulfuric acid to the filtrate from 3, boil until fumes of SO_3 appear, cool and dilute. A white precipitate of $PbSO_4$ indicates lead, but may be basic bismuth sulfate. Filter and wash.

The filtrate contains the bismuth, copper and cadmium ions along with nitrate and sulfate ions.

6. The white precipitate of 5 is strong evidence of the presence of lead. To confirm, dissolve in ammonium acetate and add potassium chromate; or, cover with K_2CrO_4 solution, add KHO in excess, then acetic acid in excess. A yellow precipitate is $PbCrO_4$.

7. Neutralize the filtrate from 5 with excess of ammonium hydroxid and heat to boiling. Bismuth hydroxid precipitates, while copper and cadmium remain in solution as complex ammonia ions, $Cu(NH_3)_4^{++}$ blue, and $Cd(NH_3)_4^{++}$ colorless. Associated with these are the nitrate and sulfate ions which have been added. If lead and mercury were not completely removed they are precipitated here. Filter.

The precipitate is $Bi(HO)_3$, proving the presence of bismuth.

The filtrate contains $Cu(NH_3)_4^{++}$ and $Cd(NH_3)_4^{++}$.

8. The precipitate of 7 is dissolved in the least possible quantity of hydrochloric acid then nearly neutralized with ammonium

hydroxid and poured into water. A white precipitate of bismuthyl chlorid, BiOCl, confirms bismuth.

9. *a.* If the filtrate from 7 is blue, copper is present; if it is colorless, copper is absent, but cadmium may be present. Even if the solution seems colorless, test a portion for copper by neutralizing with acetic acid and adding potassium ferrocyanid. A reddish brown precipitate indicates copper.

b. If copper is present, add potassium cyanid until the blue color is removed by formation of the colorless complex cyancuprous ion, $Cu_2(CN)_4^{--}$, then pass hydrogen sulfid. A yellow precipitate of CdS proves cadmium present. The cyancuprous ion is not decomposed by the H_2S, while the cyancadmium ion is. If the precipitate is dark, bismuth and lead have not been completely removed. In this case, dissolve in a little nitric acid and repeat the process from 5 to 7.

c. If copper is not present the use of the potassium cyanid is omitted and the hydrogen sulfid added at once.

D. Separation of the Ions of Group 2B, Tin Group

10. The filtrate from 2 may contain the ammonium thiosalts, more or less ionized, of any of the metals of the tin group. The anions which may be present are AsS_3^{---}, AsS_4^{---}, SbS_3^{---}, SbS_4^{---}, SnS_2^{--}, SnS_3^{--}. Add hydrochloric acid drop by drop to acid reaction, warm gently and shake well. The thioanions are decomposed and the sulfids are precipitated, mainly as the higher sulfids, along with more or less sulfid. Filter and wash with hot water containing about one per cent. ammonium chlorid throwing the filtrate away. To tell whether the precipitate is all sulfur, transfer a small portion to a test-tube and shake it with petroleum ether or benzine. If solution is complete, only sulfur is present; if there is a residue, the precipitate is treated as below the sulfur not interfering with the reactions.

11. Transfer the precipitate of 10 to flask or beaker, cover with 5 to 10 cc. concentrated hydrochloric acid, heat nearly to boiling, best by immersing in a vessel of boiling water, and shake well for several minutes. The sulfids of antimony and tin dissolve as chlorids. A little arsenic may also go into solution and,

if the quantity present is small, it may escape detection here. In order to reprecipitate this arsenic, add a quantity of water equal to that of the acid used, heat nearly to boiling and pass hydrogen sulfid for some time. A little antimony sulfid may escape solution, but will not interfere with the arsenic reactions. Filter, wash first with dilute hydrochloric acid then with hot water and boil off hydrogen sulfid from the filtrate.

The residue is As_2S_3 or As_2S_5.

The filtrate may contain Sb^{+++} (by reduction) and Sn^{++++}.

12. *a.* Dissolve a portion of the residue of 11 by boiling with nitric acid, whereby arsenate ion, AsO_4^{---}, is formed, expel excess of acid with heat, filter if necessary, add ammonium hydroxid to alkalin reaction, add magnesia mixture and shake vigorously. A white crystallin precipitate of magnesium ammonium arsenate, $MgNH_4AsO_4$, confirms arsenic.

b. Shake another portion of the residue of 11 with a 10 per cent. solution of ammonium carbonate, filter and neutralize the filtrate with dilute hydrochloric acid. Yellow precipitate of the sulfid confirms arsenic.

13. *a.* Place a few drops of the boiled filtrate of 11 on platinum foil and add a strip of tin. A dark stain on the platinum is antimony. See under Division Reagent, page 89.

b. To a portion of the filtrate of 11 add some pure iron wire and heat until the solution is colorless or of a greenish tint. Stannic is reduced to stannous ion and antimony is displaced from solution. Filter and wash, rejecting the washings.

c. Into another portion of the filtrate of 11 introduce strips of zinc and platinum in contact with one another. A black stain on the platinum appearing at once indicates antimony. Let the action continue until the evolution of hydrogen ceases, when both antimony and tin will have been displaced. Pour off the liquid and remove the zinc, scraping off with the platinum any deposit that may adhere to it, then add concentrated hydrochloric acid and boil. Tin dissolves as stannous ion and the antimony remains. Filter and wash.

14. Dissolve the displaced antimony of 13 in a solution of tartaric acid, to which a little nitric acid has been added and pass hydrogen sulfid. Yellow Sb_2S_3 confirms antimony.

15. To the filtrate of 13 add mercuric chlorid. A white precipitate finally turning gray is mercurous chlorid Hg_2Cl_2, or mercury formed by the reducing action of stannous chlorid and proves the presence of tin.

16. To the filtrate of *2b* add sodium acetate and acetic acid and pass hydrogen sulfid, filter, wash.

The precipitate in Sb_2S_5 and SnS_2.

The filtrate contains the thio- and oxyanions of arsenic.

17. To the filtrate of 16 add hydrochloric acid and pass hydrogen sulfid. Yellow As_2S_3 confirms arsenic.

18. Dissolve the precipitate of 16 in hydrochloric acid and potassium chlorate, expel chlorin and separate antimony and tin as under 13 on page 94.

TABLE FOR GROUP 2

Metals: A. Mercuric mercury, lead, bismuth, copper, cadmium.
B. Arsenic, antimony, tin.

Ions: A. Hg^{++}, Pb^{++}, Bi^{+++}, Cu^{++}, Cd^{++}.
B. As^{+++}, As^{+++++}, Sb^{+++}, Sb^{+++++}, Sn^{++}, Sn^{++++}.

Group reagent: Hydrogen sulfid with hydrochloric acid, or sulfid ion in presence of hydrogen ion.

1. Group Precipitation

Prepare solution and use reagent as directed, filter and wash.

Filtrate contains the ions of Groups 3, 4, 5 and 6.

Precipitate: A. Hgs, PbS, Bi_2S_3, CuS, CdS.
B. As_2S_3, As_2S_5, Sb_2S_3, Sb_2S_5, SnS, SnS_2.

2. Separation of Divisions A and B

a. Cover the precipitate of 1 with NH_4OH, pass H_2S, (or digest with yellow ammonium sulfid), filter, wash.

b. Treat precipitate with 3N Na_2CO_3 and 3 per cent. H_2O_2, heat to 50°, dilute, pass H_2S, filter, wash.

Filtrate contains, along with ammonium ions and excess of ammonium sulfid, the thioanions of arsenic, antimony and tin.

Residue: HgS, PbS, Bi_2S_3, CuS, CdS.

3. Separation of the Sulfids of Group 2A, Copper Group

Warm the residue of 2 with dilute nitric acid, filter and wash.

Residue HgS and $Hg(NO_3)_2$,-2HgS. Heat with aqua regia, treat with $SnCl_2$. White or gray Hg_2Cl_2 and Hg confirms **mercury.**	Solution contains Pb^{++}, Bi^{+++}, Cu^{++}, Cd^{++}, NO_3^-. Concentrate, add dilute H_2SO_4, filter, wash.		
	Precipitate $PbSO_4$. Dissolve in ammonium acetate and add K_2CrO_4. Yellow $PbCrO_4$ confirms **lead.**	Filtrate Bi^{+++}, Cu^{++}, Cd^{++}, NO_3^-, SO_4^-. Make alkalin with NH_4OH, filter, wash.	
		Precipitate $Bi(HO)_3$. Dissolve in HCl, dilute. White BiOCl confirms **bismuth.**	Filtrate $Cu(NH_3)_4^{++}$ and $Cd(NH_3)_4^{++}$. **Blue color confirms copper. Add KCN until colorless then H_2S. Yellow CdS confirms cadmium. If copper is absent add H_2S without KCN.**

4. Separation of the Sulfids of Group 2B

Add to the filtrate of 2 dilute hydrochloric acid drop by drop to acid reaction, warm gently, filter, wash. Sulfids of arsenic, antimony and tin precipitated. Transfer to a flask, cover with HCl, warm and shake. Add 40 cc. of 5 N HCl, boil and pass H_2S. Filter, wash with dilute HCl.

Residue As_2S_3, As_2S_5 and S. *a*. Dissolve in fuming HNO_3, neutralize with NH_4OH, add magnesia mixture. White crystallin $MgNH_4AsO_4$ indicates **arsenic.** *b*. Shake with ammonium carbonate, filter, neutralize with dilute HCl. Yellow sulfid confirms **arsenic.**	Filtrate contains the ions of **antimony and tin.** Boil off H_2S and divide into two **parts.**		
	a. Add iron wire and boil. Black deposit indicates **antimony.** Dissolve in tartaric acid with a little HNO_3 and pass H_2S. **Yellow** Sb_2S_3, confirms **antimony.**	*b*. **Introduce platinum and zinc. Black stain on Pt is antimony. When action ceases remove the Zn. Treat precipitate with HCl, filter or decant and add $HgCl_2$. White Hg_2Cl_2 indicates tin.**	

Chapter VIII

GROUP 3. IRON GROUP

Iron, Chromium, Aluminum

Properties and Reactions of the Metals and Ions of Group 3

IRON

The Metal.—Iron is a white or steel-gray metal, strong, tenacious, malleable, ductile, of specific gravity 7.88. It softens in the furnace, welds at white heat, and melts above 1,800°. It is unchanged in dry air, but rusts in moist air or in contact with air and water, becoming coated with ferric hydroxid, $Fe(HO)_3$. It dissolves in dilute acids evolving hydrogen, but is insoluble in alkalis. It burns in oxygen at red heat to Fe_2O_3 and Fe_3O_4, and in sulfur to FeS.

There are three principal varieties of iron whose differences depend mainly upon the quantity of carbon which they contain viz.:

Cast iron, 3 to 6 per cent. of carbon.

Steel, 0.6 to 2 per cent. of carbon.

Wrought iron, less than 0.6 per cent. of carbon.

Iron forms many alloys, the more important of which are those of zinc (galvanized iron), tin (tin plate), nickel (nickel plate), and manganese (spiegeleisen).

Iron Compounds.—Iron is quite active and forms numerous compounds. It exhibits valences two, three, four and six. It is mainly basic, but there are a few ferrates, which are unstable and will not be met with in the course of analysis. It unites with the negative elements generally and forms salts with most of the acids. The halids and salts are generally soluble in water, while the oxids, hydroxids and sulfids are insoluble. Its compounds are soluble in acids almost without exception.

Iron Ions.—There are two basic ions of iron, ferrous ion, Fe^{++}, which is nearly colorless and yields pale green salts, and ferric ion, Fe^{+++}, which has a faint reddish color and whose salts are red. The former is easily oxidized to the latter and the reverse action takes place in presence of reducing agents. Iron forms several complex anions, the most important of which are ferrate ion, FeO_3^{--}, ferrocyanid ion, $Fe(CN)_6^{----}$, and ferricyanid ion, $Fe(CN)_6^{---}$. There are also haloferrates. All these must be decomposed and converted into ferric ion before the iron is precipitated in Group 3.

Iron ions are strong, they hold the electric charge firmly and are not easily reduced to the metallic state. For this reason iron displaces from solution many metallic ions, such as those of silver, mercury, antimony, bismuth, copper, gold, platinum.

Ferrous Reactions.—Use a freshly prepared 0.1 normal solution of ferrous sulfate, $FeSO_4$, $7H_2O$, equivalent 40; or of ferrous ammonium sulfate, $Fe(NH_4)_2(SO_4)_2,6H_2O$, equivalent 98. The solution soon turns red because of oxidation of ferrous to ferric ion. This may be prevented by adding a few drops of sulfuric acid. In order that the ferrous reactions may be typical, ferric ion must be absent. The solution may be freed from this ion by the reducing action of nascent hydrogen. To a portion of the solution in a test-tube add a little dilute sulfuric acid and iron filings in excess. Stop loosely and warm until hydrogen ceases to come off.

*1. **Ammonium hydroxid** precipitates ferrous hydroxid, $Fe(HO)_2$, whose color is first nearly white, then greenish-gray and finally brown, the change of color being due to oxidation of ferrous to ferric hydroxid. The precipitation is incomplete because of separation of ammonium ion, which reduces the dissociation of the ammonium hydroxid. The precipitate dissolves in acids and with alkali hydroxids turns back, becoming Fe_3O_4. Ammonium chlorid hinders the precipitation, the soluble complex ammonium chlorferrite, $(NH_4)_2FeCl_4$, being formed. On exposure to the air this oxidizes to ferric hydroxid. One liter of water dissolves about 0.07 gram $Fe(HO)_2$.

2. **Alkali hydroxids** precipitate white ferrous hydroxid, which rapidly oxidizes to red ferric hydroxid. In the presence of ammonium chlorid the action is like that of ammonium hydroxid.

3. **Alkali carbonates** (Na_2CO_3, K_2CO_3) precipitate white ferrous carbonate, $FeCO_3$, which in contact with the air turns green, then brown, because of hydrolysis and oxidation with formation of ferric hydroxid and carbon dioxid.

$$2FeCO_3 + 3H_2O + O = 2Fe(HO)_3 + 2CO_2.$$

Ferrous carbonate is soluble in dilute acids and in ammonium carbonate. It dissolves in carbonated water to the soluble hydrocarbonate, $FeH_2(CO_3)_2$, in which form it is found in chalybeate springs. One liter of carbonated water dissolves 0.073 gram $FeCO_3$.

4. **Ammonium carbonate** precipitates white ferrous carbonate soluble in excess to unstable ferrous ammonium carbonate, $Fe(NH_4)_2(CO_3)_2$, which soon falls as ferric hydroxid.

5. **Hydrogen sulfid** precipitates from neutral or alkalin solutions black ferrous sulfid, FeS, insoluble in alkalis and alkali sulfids; easily soluble in dilute acids, even acetic. In neutral solutions the precipitation is soon stopped because of liberation of hydrogen ion,

$$Fe^{++} + H_2S \rightleftharpoons FeS + 2H^+.$$

In acid solutions there is, of course, no precipitate. Ferrous sulfid oxidizes in the air to ferrous sulfate and basic ferrous sulfate. It dissolves in water 0.006 gram to the liter.

*6. **Ammonium sulfid** precipitates completely the black ferrous sulfid,

$$Fe^{++} + (NH_4)_2S = FeS + 2NH_4^+.$$

7. **Potassium cyanid** precipitates brown ferrous cyanid, $Fe(CN)_2$, soluble in large excess to the complex ferrocyanid ion, $Fe(CN)_6^{----}$. This ion is quite stable and does not give ferrous reactions.

8. **Potassium thiocyanate**, KCNS, produces no color in pure ferrous solutions (difference from ferric ion). The solution must contain no ferric ion, otherwise a reddish color appears.

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9. **Potassium ferrocyanid,** $K_4Fe(CN)_6$, away from the air gives with pure ferrous solutions a white precipitate of potassium ferrous ferrocyanid, $K_2FeFe(CN)_6$, or of ferrous ferrocyanid, $Fe_2Fe(CN)_6$, according as one or the other reacting substance is in excess. The precipitate soon assumes a light blue color because of oxidation to ferric ferrocyanid, $Fe_4(FeC_6N_6)_3$, (Prussian blue). These compounds are all insoluble in dilute acids somewhat soluble with decomposition in alkali and ammonium hydroxids.

*10. **Potassium ferricyanid,** $K_3Fe(CN)_6$, gives a dark blue precipitate of ferrous ferricyanid, $Fe_3(FeC_6N_6)_2$, known as Turnbull's blue, insoluble in dilute acids, soluble in concentrated acids, decomposed by alkalis with separation of ferrous hydroxid.

11. **Phosphate ion,** PO_4^{---}, precipitates greenish ferrous phosphate, soluble in acids and in ammonium hydroxid, decomposed by alkalis with separation of ferrous hydroxid.

12. **Oxidizing agents** (HNO_3, Cl, Br,) with gentle heat convert ferrous into ferric ion completely.

Ferric Reactions.—Use 0.1 N solution of ferric chlorid, $FeCl_3$, $6H_2O$, equivalent 90; or of ferric nitrate, $Fe(NO_3)_3, 9H_2O$, equivalent 135.

*1. **Hydroxid ion** (NH_4OH, NaHO, KHO,) precipitates reddish brown ferric hydroxid, $Fe(HO)_3$, insoluble in excess (difference from $Al(HO)_3$, $Cr(HO)_3$ $Zn(HO)_3$, and so forth), and in ammonium chlorid; soluble in dilute acids. Ferric hydroxid loses water on being heated and forms a series of metahydroxids, and finally ferric oxid, Fe_2O_3. It is insoluble in alkali hydroxids and hence may be said to be wholly basic. There are, however, a few ferrites and ferrates which must be formed indirectly.

The precipitation of ferric hydroxid is hindered or prevented by the presence of the anions of certain organic acids such as oxalate, tartrate, citrate ions, as well as by other organic substances. These must be destroyed before the precipitation. This is best done by evaporation and ignition.

2. **Carbonate ions** (Na_2CO_3, K_2CO_3, $(NH_4)_2CO_3$, $BaCO_3$) precipitate brown basic ferric carbonate, which is at once more or

less completely decomposed by hydrolysis into ferric hydroxid and carbon dioxid,

$$2FeHOCO_3 + 2H_2O = 2Fe(HO)_3 + 2CO_2.$$

If barium carbonate is used it is added in powder and shaken with the solution.

*3. **Alkali and ammonuim acetates** give in cold solution a brown coloration due to ferric acetate, $Fe(C_2H_3O_2)_3$. When the solution is boiled, basic ferric acetate, $FeHO(C_2H_3O_2)_2$ or $Fe(HO)_2C_2H_3O_2$ or compounds still more complex, is formed by hydrolysis and precipitates,

$$Fe^{+++} + 3C_2H_3O_2^- + H_2O \rightleftharpoons FeHO(C_2H_3O_2)_2 + HC_2H_3O_2.$$

When the solution cools, the action reverses and the precipitate dissolves. Alcohol and organic acids prevent or hinder this precipitation.

*4. **Sodium phosphate**, Na_2HPO_4, precipitates yellowish white ferric phosphate, $FePO_4$, soluble in inorganic acids, insoluble in acetic acid, in ammonium hydroxid and in alkali hydroxids (difference from $AlPO_4$),

$$FeCl_3 + 2Na_2HPO_4 = 3NaCl + NaH_2PO_4 + FePO_4.$$

The precipitation is not complete, because of the presence of hydrogen ion from the sodium dihydrogen phosphate. By adding sodium acetate this ion is driven into combination with the acetate ion to form acetic acid, which does not dissolve ferric phosphate. In this way all the iron and all the phosphorus are removed from the solution,

$$FeCl_3 + Na_2HPO_4 + NaC_2H_3O_2 = 3NaCl + HC_2H_3O_2 + FePO_4.$$

Ferric phosphate is also completely precipitated by sodium ammonium phosphate (obtained by exactly neutralizing sodium phosphate with ammonium hydroxid), hydrogen ion not being present in this case,

$$Na_2NH_4PO_4 + FeCl_3 = 2NaCl + NH_4Cl + FePO_4.$$

*5. **Nascent hydrogen** reduces ferric to ferrous ion, as when zinc is placed in acid ferrous solutions.

6. **Hydrogen sulfid** reduces ferric to ferrous ion with liberation of sulfur, but ferrous sulfid cannot be precipitated because of the presence of hydrogen ion formed by the reaction,

$$2Fe^{+++} + H_2S = 2Fe^{++} + 2H^+ + S.$$

If the solution is sufficiently alkalin to neutralize the acid, black ferrous sulfid is thrown down.

*7. **Ammonium sulfid** (or polysulfid) precipitates black ferric sulfid, Fe_2S_5, (*Am. Chem. Jr.* 29, 304),

$$2Fe^{+++++} + 5\,(NH_4)_2S = Fe_2S_5 + 10NH_4^+.$$

Alkali sulfids and polysulfids act in the same way.

8. **Cyanid ion** (KCN) precipitates by hydrolysis reddish brown ferric hydroxid, $Fe(HO)_3$, which dissolves in excess to ferricyanid ion,

$$Fe\,(HO)_3 + 6CN^- = Fe\,(CN)_6^{---} + 3HO^-.$$

*9. **Potassium ferrocyanid** gives an intensely blue precipitate of ferric ferrocyanid (Prussian blue), $Fe_4(FeC_6N_6)_3$, insoluble in dilute acids, soluble in oxalic acid, decomposed by alkali hydroxids with separation of ferric hydroxid. It is not precipitated in the presence of tartrates.

10. **Potassium ferricyanid** gives a brown coloration, but no precipitate, ferric ferricyanid being soluble in water.

*12. **Potassium thiocyanate,** KCNS, gives a deep red color due to soluble ferric thiocyanate, $Fe\,(CNS)_3$. This reaction is very sensitive, but must be used with care, since many other substances interfere (mercuric salts, alkali, fluorid, sodium acetate, sodium sulfate).

Dry Reactions for Iron.—*a.* Iron compounds may be reduced on charcoal with sodium carbonate before the blow-pipe. A gray metallic iron is obtained which can be separated from the coal with a magnet.

b. The borax bead heated with an iron salt in the oxidizing flame is yellow or brown when hot and of a lighter color or colorless when cold. In the reducing flame it is green.

***Distinction Between Ferrous and Ferric Ions.**—These ions are easily distinguished by the color of the precipitates which they

form with certain reagents especially with hydroxid and ferrocyanid ions. Ferrous ion gives greenish ferrous hydroxid and white ferrous ferrocyanid, while ferric ion yields red ferric hydroxid and blue ferric ferrocyanid.

CHROMIUM

The Element Chromium.—Chromium is a gray or white crystallin solid of specific gravity 6.8. It is insoluble in water and in nitric acid but dissolves in hydrochloric acid and in warm dilute sulfuric acid. It burns in oxygen to Cr_2O_3 and in chlorin to $CrCl_3$.

Chromium Compounds.—Chromium is both basic and acidic. With its lowest valence two it is only basic forming chromous compounds, which are unstable and easily oxidized to compounds in which the valence is higher. With the valence three it is mainly basic, forming chromic compounds, but also weakly acidic yielding a few chromites. With the valence six it is wholly acidic forming chromates and dichromates. In the perchromates the valence is seemingly seven.

Ions of Chromium.—Chromium forms two elemental positive ions, chromous ion Cr^{++} blue and chromic ion Cr^{+++} purple, and one basic complex ion CrO^{++} (chromyl) in which the chromium has the valence four. The anions of chromium are chromite ion $Cr_2O_4^{--}$ green, chromate ion CrO_4^{--} yellow, dichromate ion $Cr_2O_7^{--}$ red, and perchromate ion CrO_4^{-} blue. Chromous ion is easily oxidized to chromic ion and hence is a reducing agent. The anions are readily reduced to chromic ion and hence are oxidizing agents. It is because of this easy oxidation and reduction that the student meets with none but chromic ions in the course of the analysis. The kations of chromium have a high heat of formation, are quite stable and are not easily reduced to the metallic state.

Oxidation of Chromium Compounds.—Chromous becomes chromic ion by simple exposure to the air.

Oxidizing agents convert chromic into chromate ion.

a. By fusion on platinum with potassium nitrate and sodium carbonate the yellow color indicating a chromate.

b. By heating with sodium peroxid, or with other peroxids in the presence of alkali hydroxid,

$$2Cr(HO)_3 + 3Na_2O_2 = 2Na_2CrO_4 + 2NaHO + 2H_2O.$$

$$2Cr(HO)_3 + 4KHO + 6MnO_2 = 2K_2CrO_4 + 3Mn_2O_3 + 5H_2O.$$

c. By action of bromin water in presence of alkali hydroxid,

$$Cr^{+++} + 8HO^- + 3Br \rightleftharpoons CrO_4^{--} + 4H_2O + 3Br^-.$$

Chromate ion is further oxidized to perchromate ion by action of hydrogen peroxid. This test for chromates is very delicate and may be made as follows: A few drops of hydrogen peroxid or a few particles of sodium peroxid are added to some of the solution in a test-tube with a little hydrochloric acid. If chromate or dichromate ion is present, the solution assumes the deep blue color of the perchromate ion. See hydrogen peroxid.

Reduction of Chromium Compounds.—Chromates and dichromates are easily reduced to chromic compounds in many ways, of which the following are examples:

a. By action of sulfurous acid, (Na_2SO_3 and HCl).

b. By action of hydrochloric acid.

c. By many organic substances such as oxalic acid and alcohol. In all cases the reduction is made evident by the change of color from yellow or red to green. Because of the above reductions the chromates and dichromates are rather powerful oxidizing agents.

Chromic is reduced to chromous ion by the action of nascent hydrogen as when zinc and sulfuric acid are added to chromic solution.

Chromic Reactions.—Since chromous compounds are easily oxidized and since chromates and dichromates are reduced by hydrochloric acid and hydrogen sulfid, it is in the chromic condition that the student will always find the chromium.

Use 0.1 N solution of chrome alum, $KCr(SO_4)_2,12H_2O$, equivalent 124.5.

*1. **Ammonium hydroxid** precipitates greenish gray chromic hydroxid, $Cr(HO)_3$, (or basic hydroxids) somewhat soluble in excess to a violet colored solution which contains complex chro-

mic ammonium compounds. These last are decomposed by boiling and the hydroxid is completely precipitated. Organic acids interfere with the precipitation as in the case of aluminum. Chromic hydroxid is soluble in acids and in alkali hydroxids, thus acting both as base and as acid.

*2. **Alkali hydroxids** (NaHO, KHO) precipitate chromic hydroxid, soluble in excess with formation of the green chromite,

$$Cr^{+++} + 4HO^- \rightleftharpoons CrO_2^- + 2H_2O.$$

The chromite ion is weakly acidic and on heating the solution it undergoes hydrolysis so that the above reaction is reversed.

3. **Alkali and ammonium acetates** in boiling solutions precipitate basic chromic acetate $CrHO(C_2H_3O_2)_2$, just as in the case of iron and aluminum. The precipitate redissolves on cooling.

4. **Carbonate ions** ($BaCO_3$, Na_2CO_3) precipitate a mixture of hydroxid and basic carbonate soluble in acids.

*5. **Ammonium sulfid and alkali thiosulfates** precipitate by hydrolysis chromic hydroxid insoluble in excess.

6. **Phosphate ions** precipitate greenish chromic phosphate, $CrPO_4$, soluble in acids.

7. **Dry Reactions.**—*a*. When chromium compounds are heated with borax bead, yellow sodium chromium borate, $Na_6Cr_2(BO_2)_{12}$, is formed.

b. Heated on platinum with fusion mixture (Na_2CO_3 and KNO_3) or with sodium peroxid, chromium compounds yield yellow sodium chromate, Na_2CrO_4.

To Distinguish the Conditions of Chromium.—It may be desirable to determine the condition of the chromium in the original substance. This can usually be done by means of the color and a few simple tests. The ions have the characteristic colors already given.

In aqueous solution both chromates and dichromates hydrolize, the former becoming alkalin and the latter acid,

$$2CrO_4^{--} + H_2O \rightleftharpoons Cr_2O_7 + 2HO^-,$$
$$Cr_2O_7 + H_2O \rightleftharpoons 2CrO_4 + 2H^+.$$

A chromate solution will therefore contain both chromate and dichromate ions.

ALUMINUM

The Metal.—Aluminum is a bluish white, malleable ductile metal of specific gravity 2.58. It melts at 700° and crystallizes on cooling in octohedrons. It tarnishes but slightly in the air, is not attacked by water, is quite soluble in hydrochloric acid, less so in sulfuric acid, almost insoluble in nitric acid. The action of nitric acid is stopped by the formation of a coating of Al_2O_3, which protects the metal beneath. Aluminum burns to Al_2O_3, a substance which is scarcely attacked by acids.

Aluminum Compounds.—Aluminum unites directly to the negative elements forms salts with most of the acids, and yields alloys with many of the metals. Its double sulfates (the alums) and its silicates (clay, feldspar, beryl, etc.,) are characteristic compounds. The oxid occurs native as corundum the hardest of all substances except the diamond. Of aluminum compounds the oxid, hydroxid, silicate, arsenate and arsenite are insoluble in water, while most of the other compounds are more or less soluble.

Aluminum Ions.—Aluminum is strictly trivalent. It forms one elemental ion, Al^{+++}, which is colorless and quite active. It dissolves in strong hydroxids to form aluminate ion, AlO_3^{---}, and combines with the halogens to haloaluminate ions such as AlF_6^{---}. Aluminum is, therefore, both acidic and basic, but mainly basic. The aluminum ion is strong, possessing little tendency to pass to the molecular state and aluminum compounds are reduced with difficulty.

Soluble compounds of aluminum hydrolize rather freely, the salts becoming acid, and the aluminates becoming alkalin with separation of aluminum hydroxid,

$$Al^{+++} + 3H_2O \rightleftharpoons AlO_3^{---} + 6H^+.$$

$$AlO_3^{---} + 3H_2O \rightleftharpoons Al(HO)_3 + 3HO^-.$$

Aluminum Reactions.—Use 0.1 N solution of common alum, $KAl(SO_4)_2$, $12H_2O$, equivalent 118.5; or of aluminum chlorid, $AlCl_3 6H_2O$, equivalent 80.5.

*1. **Ammonium hydroxid** precipitates white gelatinous alumi-

num hydroxid $Al(HO)_3$, a portion of which remains in colloidal solution. The precipitation is complete in the presence of ammonium salts,

$$AlCl_3 + 3NH_4OH = Al(HO)_3 + 3NH_4Cl.$$

Colloidal substances like aluminum hydroxid may exist in a soluble form as **hydrosol** and in an insoluble form as **hydrogel.** The hydrosol is usually changed to hydrogel by boiling but the change is more complete in the presence of salts, especially ammonium salts.

Freshly precipitated aluminum hydroxid is quite soluble in dilute acids, but on long contact with water or after boiling it is converted into the difficultly soluble metahydroxids, $Al_2O(HO)_4$ and AlOHO.

Aluminum hydroxid forms with acids aluminum salts and with strong alkalis aluminates. Ammonium hydroxid dissolves it slightly, but the concentration of the ammonium aluminate formed must remain small because of the tendency of this compound to hydrolize and because of the basic weakness of ammonium hydroxid,

$$Al(HO)_3 + 3NH_4OH \rightleftharpoons (NH_4)_3AlO_3 + 3H_3O.$$

If an ammonium salt is present the dissociation of the ammonium hydroxid is practically reduced to zero, because of the increase of ammonium ions, and the reaction goes backward until the precipitation of aluminum hydroxid is complete. This explains the use of ammonium chlorid in the precipitation of the ions of this group.

Aluminum hydroxid is soluble in neutral alkali tartrates as well as in other organic compounds such as malates, citrates, sugar and starches, forming with them complex ions, and so these substances hinder or prevent the precipitation.

*2. **Alkali hydroxids** (NaHO, KHO) precipitate aluminum hydroxid soluble in excess as explained in the last paragraph. Dilute acids reprecipitate the hydroxid, which dissolves again on addition of more acid.

3. **Carbonate ions** (Na_2CO_3, K_2CO_3, $(NH_4)_2$, CO_3) precipitate the hydroxids by hydrolysis.

*4. **Barium carbonate** in fine powder shaken with an aluminum solution precipitates aluminum hydroxid with liberation of carbon dioxid. This is again because of the hydrolysis of the small quantity of barium carbonate which goes into solution and of the aluminum carbonate which is probably first formed,

$$2AlCl_3 + 3BaCO_3 + 3H_2O = 3BaCl_2 + 2Al(HO)_3 + 3CO_2.$$

If sulfate ion is present, barium sulfate will be mixed with the hydroxid.

5. **Ammonium sulfid** precipitates by hydrolysis aluminum hydroxid with evolution of hydrogen sulfid,

$$2Al^{+++} + 3(NH_4)_2S + 6H_2O = 2Al(HO)_3 + 3H_2S + 6NH_4^+.$$

6. **Alkali phosphates** precipitate aluminum phosphate, $AlPO_4$, insoluble in acetic acid, soluble in inorganic acids, and in alkali hydroxids in the absence of ammonium chlorid.

7. **Cyanid ion** precipitates aluminum hydroxid by hydrolysis,

$$3CN^- + Al^{+++} + 3H_2O = Al(HO)_3 + 3HCN.$$

8. **Alkali and ammonium acetates** produce no perceptible change in cold neutral solutions, aluminum acetate which is formed, $Al(C_2H_3O_2)_3$, being soluble. At the boiling temperature basic aluminum acetate is formed by hydrolysis and falls as a white precipitate. The reaction is reversible and when the mixture cools the precipitate redissolves,

$$Al^{+++} + 2C_2H_3O_2^- + 2H_2O \rightleftharpoons Al(HO)_2C_2H_3O_2 + HC_2H_3O_2.$$

In the presence of alkali hydroxids the precipitate is not formed, even in hot solution (difference from iron and chromium).

9. **Dry Reactions.**—When heated in the air compounds of aluminum are decomposed with formation of the oxid. If this is moistened with cobalt nitrate and strongly heated again, the mass becomes blue from formation of cobalt aluminate, $Co(Al_2)_2$, (Thenard's blue). Metallic oxids mask the color.

Analysis of the Iron Group

SEPARATION AND IDENTIFICATION OF THE METALS AND IONS OF GROUP 3

Metals other than those of Groups 1 and 2, whose hydroxids are insoluble in ammonium hydroxid in presence of ammonium chlorid.

Metals: Iron, chromium, aluminum.

Ions: Fe^{++}, Fe^{+++}, Cr^{+++}, Al^{+++}.

Group reagent: Ammonium hydroxid in presence of ammonium chlorid.

The metals of this group are both acidic and basic, forming anions as well as kations. For their proper precipitation it is necessary that all should be present as kations and that iron and chromium should be in the trivalent state. The change will generally have been effected by the reagents of Groups 1 and 2, but sometimes special treatment will be necessary as will be explained on page 112.

Principle.—The kations of this group combine with hydroxid ion to form hydroxids, which are insoluble in water in dilute alkalis, and in excess of ammonium hydroxid.

Group Reagent.—Ammonium hydroxid is used as the group reagent because, being slightly ionized, its solvent action is small. Its solvent power is further diminished by ammonium chlorid, the excess of ammonium ions driving the ions of ammonium hydroxid back into combination and thus reducing the number of hydroxid ions almost to zero. The ammonium chlorid prevents the precipitation of manganese and magnesium as hydroxids and the excess of ammonium hydroxid keeps zinc, nickel and cobalt in solution as complex ammonia ions. Alkali hydroxids cannot be used as group reagent, since they dissolve the hydroxids of aluminum and chromium. These hydroxids are slightly soluble in ammonium hydroxid and the reagent must be used in very slight excess.

The Precipitate.—The group precipitate consists properly of red ferric hydroxid, $Fe(HO)_3$, while aluminum hydroxid, $Al(HO)_3$, and greenish chromic hydroxid, $Cr(HO)_3$. These

are all soluble in acids, all but ferric hydroxid soluble in strong alkalis. In the presence of ammonium chlorid and a very slight excess of ammonium hydroxid the precipitation is practically complete.

When manganese is present it may be thrown down with this precipitate as manganic hydroxid. Manganous hydroxid oxidizes in contact with the air to manganic hydroxid and this is not held in solution by ammonium chlorid. It should always be looked for and is separated along with the iron. In the same way cobalt may appear here.

Substances in the Precipitate not of the Group.—Because of the presence of interfering substances the precipitate may contain other things besides the hydroxids of the metals of the group and care must be taken not to be misled by them. Those which are most commonly met with are as follows:

1. Phosphates of iron, aluminum, chromium, manganese calcium, strontium, barium, magnesium.

2. Fluorids, oxalates and sulfates of barium, strontium, calcium.

3. Silicic acid.

Interfering Substances.—When the solution is rendered alkalin by the group reagent, marked changes take place which must be carefully noted. Substances which were inert in the acid liquid now become active and either prevent the proper precipitation of the members of the group or produce other precipitates foreign to the group. When such substances are found to be present they must generally be removed before the analysis is continued. The principal interfering substances are here described.

1. **Organic substances,** espécially those containing the hydroxyl radical hinder or prevent the precipitation of the metals of this group, particularly iron and aluminum, by forming soluble complex compounds with them. Such substances are sugar, starch and salts of the organic acids.

2. **Phosphate, oxalate** and **fluorid ions** form with certain metals or ions of Groups 3, 4 and 5, salts which are insoluble in water and dilute ammonium hydroxid. Such compounds will therefore

be precipitated along with the hydroxids of iron, chromium and aluminum upon addition of the group reagent.

3. **Silicate ion**, in a solution made alkalin with ammonium hydroxid or ammonium carbonate, unites with ammonium ion to form ammonium silicate, $(NH_4)_2SiO_3$, which being a combination of weak ions, hydrolizes completely with precipitation of white gelatinous silicic acid which may be mistaken for aluminum hydroxid.

4. **Sulfate ion** may be formed by oxidation of the sulfids of Group 2, in which case the metals of Group 5 will fall as sulfates.

Tests for Interfering Substances.—Interfering substances are tested for as follows:

1. Evaporate 5 cc. of the solution to dryness in a porcelain dish and heat to 120°.

2. Remove a portion of the residue to a test-tube or dish, moisten with concentrated sulfuric acid and heat until white fumes of SO_3 appear. Carbonization and odor of burn sugar indicate **organic matters.**

3. Moisten the remainder of the residue with strong hydrochloric acid add a few cubic centimeters of water, boil and filter. The residue may contain carbon, silicic acid and insoluble sulfates. The filtrate contains phosphates, oxalates, soluble sulfates and fluorids.

4. To confirm silicic acid make a bead of microcosmic salt on a platinum wire, attach a little of the residue of 3 and heat in the Bunsen flame or with a blow-pipe. A skeleton of silica in the bead indicates **silicates.**

5. To a small portion of the filtrate of 3 add a few drops of strong nitric acid and boil, then add an equal volume of ammonium molybdate solution. A yellow precipitate of ammonium phosphomolybdate, $(NH_4)_3PO_4,12MO_3$, indicates **phosphates.**

6. To a larger portion of the filtrate of 3 add sodium carbonate to alkalin reaction and boil. The kations generally are precipitated as carbonates and the sodium salts of the acids present remain in the solution. Filter, add to the filtrate a

slight excess of acetic acid and a solution of calcium sulfate. A white precipitate of calcium oxalate, CaC_2O_4, indicates **oxalic acid** or **oxalates.**

7. The precipitate of 6 may contain calcium fluorid as well as calcium oxalate. In this case fluorin may be confirmed as follows: Place a little of the precipitate in a test-tube, dry thoroughly, add concentrated sulfuric acid and apply heat. Hold in the escaping vapors which contain SiF_4 a moistened glass rod. The moisture becomes clouded with silicic acid due to the reaction,

$$3SiF_4 + 3H_2O = 2H_2SiF_6 + H_2SiO_3.$$

Removal of Hydrogen Sulfid.—The filtrate from Group 2 is boiled until all the hydrogen sulfid is expelled, or until a strip of paper moistened with lead acetate solution is not darkened when held in the escaping vapors. Hydrogen sulfid must be removed or it will unite with the group reagent to form ammonium sulfid, which will precipitate the metals of Group 4. This boiling should be done immediately after the filtration, otherwise sulfate ion is formed by oxidation and precipitates the alkali earth metals as sulfates. If no hydrogen sulfid has been used, the boiling is not necessary.

Oxidation of Iron.—To a small portion of the boiled filtrate add a drop of potassium ferricyanid solution. A blue precipitate indicates ferrous ion and a brown or green coloration ferric ion. If iron is present add to the main solution a little nitric acid and boil for a minute. Repeat until oxidation is complete. This is to oxidize the iron to the ferric condition which is necessary since ferrous ion is not precipitated by ammonium hydroxid in the presence of ammonium chlorid. If chromous ion is present, it will become chromic ion.

Removal of Interfering Substances.—If carbonizing organic matters or oxalates are found, they must be removed. If phosphates are present, the precipitate must be so treated as to leave the kations in solutions and remove the phosphate ions. Silicate.

sulfate and fluorid ions are not likely to interfere much and are recognized as they appear in the course of the analysis.

Organic substances and silicates are removed as follows: Evaporate the solution to dryness, moisten the residue with hydrochloric acid, add a little water and evaporate to dryness again to render the silica insoluble. Raise the temperature of the dish to redness until organic matter is decomposed. Treat the residue with hydrochloric acid, boil and filter. The residue is carbon, silicic oxid and possibly sulfates. It may also contain the oxids of iron, chromium and aluminum, which were rendered insoluble by the ignition. These may be brought into solution by first fusing them with potassium persulfate. The analysis is continued with the filtrate, which is now free from organic matters and silicates. See also page 198.

If oxalates are the only organic matters present, they may be removed as follows: Boil the filtrate from Group 2 to expel hydrogen sulfid, add a few drops of nitric acid to oxidize iron, chromium and manganese, then add strong sodium carbonate solution as long as precipitate falls and boil for a few minutes. Cool, filter and wash with hot water. The precipitate may be hydroxids of iron chromium, aluminum, and manganese, and carbonates of zinc, nickel, cobalt, calcium, strontium, barium, and magnesium. Dissolve in hydrochloric acid and proceed with the analysis. The filtrate contains the oxalate ions, together with the ions of sodium, potassium, lithium and ammonium.

The Analysis.—There are two methods of separating the metals of Group 3, each of which has its advantages. The first or hydroxid method is rapid and easy and generally satisfactory, especially in the presence of phosphates, or in the absence of manganese. The second or basic acetate method requires more time, but is more accurate since the hydroxids of the following groups are less liable to fall. Furthermore the phosphates are removed without special treatment.

I. Hydroxid Method.—

1. To the filtrate from Group 2 or to the solution as prepared above, the hydrogen sulfid having been expelled and the iron oxidized, add ammonium chlorid, heat to boiling and add ammonium hydroxid in slight excess. Filter hot and reject the washings. Only enough ammonium chlorid should be present to keep the ions of the following groups in solution. A large excess will interfere with the precipitation. Ammonium chlorid is already present, being formed by the action of the reagent of this group with that of Group 1, and it may not be necessary to add more.

A. Phosphates not present.—

The filtrate may contain the ions of Groups 4, 5 and 6.

The precipitate may contain red ferric hydroxid, $Fe(HO)_3$, greenish chromic hydroxid, $Cr(HO)_3$, white aluminum hydroxid, $Al(HO)_3$, with possibly manganic hydroxid, $Mn(HO)_3$, and cobalt hydroxid, $Co(HO)_2$. If the last two are present, dissolve in HCl, add NH_4Cl and precipitate again with NH_4HO.

2. Transfer a portion of the washed precipitate to a beaker with a small quantity of water, add a little sodium peroxid and boil until effervescence ceases. The ferric hydroxid remains unchanged, (manganese hydroxid also if present) the chromic hydroxid is oxidized to sodium chromate, and the aluminum hydroxid is changed to sodium aluminate. Filter and wash.

The filtrate contains yellow chromate ion, CrO_4^{--}, and colorless aluminate ion, AlO_3^{---}. Absence of color means absence of chromium.

The residue is red ferric hydroxid, $Fe(HO)_3$. There may be also manganic hydroxid, cobalt hydroxid and certain sulfates.

If iron and chromium are present together, the filtrate is liable to contain some iron and the precipitate some chromium.

3. Dissolve the residue of 2 in hot hydrochloric acid and confirm iron by adding potassium ferrocyanid or thiocyanate. Manganese and cobalt need not be confirmed here unless a trace seems to be present and they are not found in their proper place. An undissolved residue may consist of sulfates. A blue precipi-

tate with the ferrocyanid or a red color with the thiocyanate proves the presence of iron.

4. To a portion of the filtrate from 2 add acetic acid and lead acetate. A yellow precipitate is lead chromate, $PbCrO_4$, proves the presence of chromium.

5. Treat other portions of the filtrate from 2 in one or both of the following ways: *a*. Add nitric acid to acid reaction, heat to boiling and add ammonium hydroxid to slight excess; *b*. Add ammonium chlorid to decompose the sodium hydroxid and sodium aluminate present and boil. A white precipitate is aluminum hydroxid and proves the presence of aluminum. If the chromium color interferes with the proper observation of the precipitate, filter, wash, dissolve in a little acid and precipitate again with ammonium hydroxid. For traces of aluminum see page 117.

B. Phosphates present.—

6. If phosphates are present, the precipitate thrown down by the group reagent may contain hydroxids and phosphates of iron, chromium and aluminum, and also phosphates of the metals of Groups 4 and 5, and of magnesium. The phosphate ion unites by preference to the ferric ion, and if there is an excess of the latter, the phosphate ion will all be removed, the chromium and aluminum will fall, partly at least, as hydroxids, and the metals of Groups 4 and 5 will remain in solution. If on the other hand phosphate ion is in excess, the metals of Groups 4 and 5 and magnesium may be precipitated as phosphates. In any case dissolve the precipitate in a little warm dilute hydrochloric acid, nearly neutralize with sodium carbonate to remove the excess of hydrogen ions, add a mixture of sodium acetate and acetic acid, boil gently for a time, filter and wash. The acetate ion unites with the hydrogen ion to form undissociated acetic acid and thus nullifies its solvent action.

The filtrate contains the ions of Groups 4, 5 and 6, together with the excess of phosphate ions. Treat as directed in 8.

The precipitate contains the phosphates of iron, chromium and

aluminum and also the hydroxids of these metals if there is not sufficient phosphate ion to convert them all into phosphates.

7. The precipitate of 6 is treated just as the hydroxids were beginning with 2. The sodium peroxid coverts the chromium and aluminum phosphates into chromate and aluminate ions, while the iron phosphate remains on the filter. Continue as in 3, page 114.

8. If the filtrate from 6 contains phosphate ions, they must be removed, otherwise they will precipitate the metals of Groups 4 and 5 when the solution is neutralized. Add dilute ferric chlorid solution drop by drop until a faint red color just appears, indicating the complete removal of the phosphate ion and the formation of red ferric acetate, $Fe(C_2H_3O_2)_3$. Boil the solution to change the ferric to basic ferric acetate, $FeHO(C_2H_3O_2)_2$, and filter hot, since the precipitate redissolves on cooling. The precipitate containing all the phosphorus as ferric phosphate and the remainder of the added iron as basic ferric acetate is thrown away.

The filtrate contains ions of Groups 5 and 6 and should be added to the filtrate from the group reagent 1.

II. Basic Acetate Method.—

1. The filtrate from Group 2 or the solution prepared for Group 3 is neutralized with ammonium carbonate to remove the hydrogen ion. If the precipitate formed is not red, add a few drops of ferric chlorid, dissolve the precipitate in hydrochloric acid and add ammonium carbonate again to precipitation. Repeat this process until the red color is obtained. This is in order to insure the presence of enough ferric ion to precipitate all the phosphate ion and leave a surplus to assist in the precipitation of the basic acetates. Add dilute hydrochloric acid drop by drop with shaking until the precipitate is just dissolved, then add neutral ammonium acetate in excess, pour the mixture into a large quantity (200 to 500 cc. of boiling water and continue the boiling until the red precipitate of the basic acetate separates.

Filter and wash with hot water since the basic acetates redissolves on cooling. The solution should be kept as nearly neutral as possible, since hydroxid ion causes the formation of hydroxids instead of acetates, and hydrogen ion interferes with the hydrolysis and prevents the proper formation of the basic acetates. The dilution facilitates the hydrolysis.

The filtrate contains the ions of Groups 4, 5 and 6 and is free from ion and phosphates.

The precipitate contains the basic acetates of iron, chromium and aluminum, $FeHO(C_2H_3O_2)_2$, $CrHO(C_2H_3O_2)_2$ and $AlHO(C_2H_3O_2)_2$, and ferric phosphate, $FePO_4$.

2. Treat the precipitate with sodium peroxid as in the hydroxid method, boil, filter and wash.

The residue is ferric hydroxid and has no significance because iron was added as one of the reagents.

The filtrate contains chromate ions, CrO_4, and aluminate ions, $AlO_3{---}$.

3. Identify chromium as in the hydroxid method. If phosphates are present, white lead phosphate may fall, but this need not be mistaken for the yellow lead chromate.

4. Identify the aluminum as in the hydroxid method.

If a trace only of aluminum is present, it may be confused with the compounds of aluminum and of silicic acid, which are always found in alkalin reagents which are kept in glass bottles. In this case we may proceed as follows: Transfer a portion of the precipitated basic acetates to a test-tube, add half a gram each of sodium carbonate and barium hydroxid with a few cubic centimeters of water, boil thoroughly and filter. The boiling sodium hydroxid formed by the action of the barium hydroxid on the sodium carbonate dissolves the basic aluminum acetate, leaving the chromium salt unchanged.

The filtrate contains sodium aluminate, Na_3AlO_3. Acidify with hydrochloric acid, add ammonium hydroxid in slight excess and boil. A white flocculent precipitate of aluminum hydroxid, $Al(HO)_3$, proves the presence of aluminum.

TABLE FOR GROUP 3

Prepare the solution and make the precipitation as directed above.

Metals: Iron, chromium, aluminum.

Ions: Fe^{+++}, Cr^{+++}, Al^{+++}.

Group reagent: Ammonium hydroxid with ammonium chlorid.

Filtrate contains ions of Groups 4, 5 and 6.

A. Phosphates not present.

Precipitate: $Fe(HO)_3$, $Cr(HO)_3$, $Al(HO)_3$.

Treat with Na_2O_2, boil, filter, wash.

Residue $Fe(HO)_3$. Dissolve in hot dilute HCl and add $K_4Fe(CN)_6$. Blue precipitate indicates iron.	Filtrate contains yellow chromate ion, CrO_4--, and colorless aluminate ion, AlO_3---, with sodium and hydroxid ions. Divide into two portions.	
	1. Yellow color indicates chromium. Acidify with $C_2H_4O_2$ and add $Pb(C_2H_3O_2)_2$. Yellow precipitate indicates chromium.	2. Acidify with HNO_3 and add NH_4OH. White precipitate indicates aluminum. If Cr is present the color may interfere. Filter, wash, dissolve in HNO_3 and add NH_4HO.

B. Phosphates present.

Precipitate: $FePO_4$, $CrPO_4$, $AlPO_4$, hydroxids and other phosphates. Dissolve in warm dilute HCl, nearly neutralize with Na_2CO_3, add $C_2H_4O_2$ and $NaC_2H_3O_2$, boil, filter, wash.

Precipitate: $FePO_4$, $CrPO_4$, $AlPO_4$ also possibly the hydroxids. Treat with Na_2O_2, boil, filter, wash and continue as above.	Filtrate contains phosphate tions. Add $FeCl_3$ to red color, boil, filter hot. Combine with main filtrate of Group 3 and use for remaining groups.

For basic Acetate method follow the directions on page 116.

Chapter IX

GROUP 4. ZINC GROUP

Zinc, Manganese, Cobalt, Nickel

Properties and Reactions of the Metals and Ions of Group 3

ZINC

Metallic Zinc.—Zinc is a bluish white, brittle, moderately hard metal which melts at 420°, boils at 950° and has specific gravity 7.0. It tarnishes in moist air becoming covered with basic zinc carbonate and when heated burns to zinc oxid, ZnO. It dissolves in dilute acids with evolution of hydrogen. It acts violently upon strong nitric acid decomposing it and setting free oxids of nitrogen, the hydrogen being oxidized to water.

Zinc Compounds.—Zinc is quite active. It unites directly to most of the negative elements when heated with them and forms salts with nearly all the acids. It is bivalent and basic, though with strong alkalis it has a weak acid character and forms zincates. It forms alloys with many metals the most important of which is brass, an alloy of zinc and copper.

Zinc Ions.—Zinc forms one elemental ion, Zn^{++}, which is colorless, active, basic and poisonous. The negative zincate ion, ZnO_2^{--}, occurs in connection with strong alkalis. There are also the complex zinc ammonia, halozincate and cyanzincate ions. The zinc kation is quite strong and hence zinc is not easily displaced by other metals, and for the same reason it displaces many metals from their solutions.

Reactions of Zinc Ion.—Many zinc compounds are insoluble in water, most of them are soluble in acids. Of those soluble in water the more common ones are the chlorid, sulfate and nitrate.

Use 0.05 N solution of zinc sulfate, $ZnSO_4$, $7H_2O$, equivalent 144.7.

*1. **Ammonium sulfid** precipitates from neutral or alkalin so-

lutions white colloidal zinc sulfid, ZnS, soluble in mineral acids, insoluble in alkalis and in acetic acid. The precipitate passes through the filter because it is in the hydrosol form. It may be obtained as hydrogel by precipitating hot and in the presence of ammonium salts. It dissolves in water 0.0068 gram to the liter.

*2. **Hydrogen sulfid** precipitates from neutral solutions white zinc sulfid ZnS, partially because an acid is formed and the reaction is reversible,

$$ZnSO_4 + H_2S \rightleftharpoons H_2SO_4 + ZnS.$$

The more dilute the solution the more complete will be the precipitation. Since zinc sulfid is insoluble in acetic acid it will be completely precipitated in the presence of sodium acetate, the acetate ion combining with the hydrogen ion as fast as it is set free. In alkalin solution the precipitation is complete, the hydrogen and hydroxid ions combining to form water.

*3. **Ammonium Hydroxid** precipitates from neutral or acid solutions white gelatinous zinc hydroxid, $Zn(HO)_2$, soluble in acids and in alkalis and in ammonium salts. It dissolves in excess of the precipitant with formation of the complex zinc ammonia ion, $Zn(NH_3)_n^{++}$, in which n may have several values determined somewhat by the concentration of the ammonium ions, more usually six. It is because of the formation of this ion that all zinc compounds except the sulfid and ferrocyanid are soluble in ammonium hydroxid. One liter of water dissolves at 18° 0.0013 gram $Zn(HO)_2$.

*4. **Alkali hydroxids** precipitate from neutral or acid solutions zinc hydroxid, easily soluble in excess to alkali zincates,

$$Zn(HO)_2 + 2HO^- \rightleftharpoons ZnO_2^{--} + 2H_2O.$$

On boiling the zincate solution hydrolysis takes place and the hydroxid is reformed.

5. **Carbonate ions** (Na_2CO_3, K_2CO_3, $(NH_4)_2CO_3$) precipitate basic zinc carbonate of varying composition, soluble in ammonium hydroxid to zinc ammonia ion and in acids and in alkalis. Ammonium chlorid prevents or hinders the precipitation by form-

ing soluble chlorzincates. The solubility of this precipitate in water is variable ranging from 0.5 to 0.02 gram to the liter.

6. **Hydrogen sodium carbonate** gives normal zinc carbonate, but incompletely because of liberation of hydrogen ion,

$$HNaCO_3 + Zn^{++} \rightleftharpoons ZnCO_3 + H^+ + Na^+.$$

One liter of water dissolves at 15° 0.01 gram $ZnCO_3$.

7. **Disodium phosphate** precipitates normal zinc phosphate, $Zn_3(PO_4)_2$, first gelatinous, then crystallin, soluble in acids to zinc salts and in ammonium compounds to zinc ammonia salts.

8. **Potassium cyanid** gives white zinc cyanid, $Zn(CN)_2$, soluble in acids and in alkalis and in excess of potassium cyanid, the last forming cyanzincate, $Zn(CN)_2 = 2KCN \rightleftharpoons K_2Zn(CN)_4$, which is decomposed by acids and alkalis and alkali sulfids.

9. **Potassium ferrocyanid** precipitates white or pale green zinc ferrocyanid, $Zn_2Fe(CN)_6$, insoluble in acids and in ammonium hydroxid, soluble in alkalis, converted by excess of the reagent into potassium zinc ferrocyanid, $K_2Zn_3(FeC_6N_6)_2$.

10. **Potassium ferricyanid** precipitates yellowish zinc ferricyanid, $Zn_3(FeC_6N_6)_2$, insoluble in dilute acids, decomposed but not dissolved by alkalis soluble in dilute ammonium hydroxid and in concentrated hydrochloric acid.

11. **Dry Reactions.**—Heated with sodium carbonate on charcoal, zinc compounds are reduced and the volatile zinc burns in the flame producing an incrustation of zinc oxid which is yellow when hot and white when cold. If the oxid is moistened with cobalt nitrate it assumes a green color (Rinnmann's green).

MANGANESE

The Metal.—Manganese is a steel-gray, brittle, crystallin solid with specific gravity 8, melting point, 1,900°, and hardness equal to that of glass. It tarnishes in the air and burns finally to manganese tetroxid. It dissolves in acids to manganous salts.

Manganese Compounds.—Manganese is basic in its lower and acidic in its higher valences. With valences two and three it forms manganous and manganic compounds; with valence four,

peroxid, persulfid and manganites; with valences six and seven, manganates, dimanganates and permanganates.

Ions of Manganese.—Manganese forms an unusual number of ions. There are two elemental and basic ions, pale red manganous, Mn^{++}, and violet manganic, Mn^{+++}. The more important anions of manganese are brown manganite, MnO_3^{--}, green manganate, MnO_4^{--}, violet permanganate, MnO_4^{-}, purple manganocyanid, $Mn(CN)_6^{----}$, red manganicyanid, $Mn(CN)_6^{---}$. All the ions of manganese are highly colored except manganous ion which in dilute solution is almost colorless.

***Oxidation of Manganese Compounds.**—Dry manganous compounds except the hydroxid do not oxidize in the air. Oxidizing agents convert them into manganic compounds and then into manganates and permanganates. If for example, a manganous salt is fused on platinum with sodium carbonate and potassium nitrate, a soluble green sodium manganate is formed. Moist manganates change in the air to permanganates, rapidly in the presence of acids.

Manganous ions in neutral solution in contact with the air oxidize and precipitate as brown manganic hydroxid, the solution becoming acid. Acids retard and hydroxids promote the reaction which is thus shown to be reversible and may be represented as follows:

$$2Mn^{++} + 5H_2O + O \rightleftharpoons 2Mn(HO)_3 + 4H^{+}.$$

In the presence of alkali hydroxids which remove the hydrogen ion as fast as it is set free and of more powerful oxidizing agents such as chlorin, bromin and hydrogen peroxid, manganese dioxid precipitates,

$$Mn^{++} + O + H_2O + 2HO^{-} = MnO_2 + 2H_2O.$$

***Reduction of Manganese Compounds.**—Manganese dioxid and manganates and permanganates are unstable giving up the oxygen readily and are therefore strong oxidizing agents. They are reduced by almost all hydrogen compounds. Potassium permanganate is especially active, two molecules yielding in acid solution five atoms of available oxygen with reduction to man-

ganous ion, while in neutral or alkalin solution three atoms of oxygen are available and manganese dioxid is precipitated. The following equations are taken as examples:

a. Manganese dioxid and hydrochloric acid,

$$MnO_2 + 2HCl = MnCl_2 + H_2O + O.$$

b. Potassium manganate and sulfuric acid,

$$K_2MnO_4 + 2H_2SO_4 = K_2SO_4 + MnSO_4 + 2H_2O + O_2.$$

c. Potassium permanganate and sulfuric acid,

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O.$$

d. Potassium permanganate in alkalin solution,

$$2KMnO_4 + H_2O = 2MnO_2 + 2KHO + 3O.$$

Potassium permanganate is much used for oxidation of substances in solution; as for example, sulfite to sulfate ion, ferrous to ferric ion, oxalic acid to carbon dioxid and water, and organic matters generally.

Potassium permanganate serves as its own indicator since its reduction involves the discharge of its color. When permanganate is added to a solution the color is discharged as long as oxidation continues; when the color persists the oxidation is complete.

Manganese Reactions.—At this stage of the analysis all manganese compounds will have been reduced by the action of hydrochloric acid and hydrogen sulfid, the reagents of Groups 1 and 2, and it will only be necessary to study the reactions of manganous ion.

Use 0.05 N solution of manganous chlorid, $MnCl_2, 4H_4O$, equivalent 99; or of manganous sulfate, $MnSO_4, 5H_2O$, equivalent 120.5.

*1. **Ammonium sulfid** precipitates from neutral or alkalin solutions pinkish white manganous sulfid, MnS, easily soluble in dilute acids (distinction from cobalt and nickel), even in acetic acid (distinction from zinc). The precipitate is more or less hydrated. The separation is complete even in the presence of ammonium chlorid. One liter of water dissolve 0.0063 gram MnS.

*2. **Hydrogen sulfid** does not precipitate manganese from neutral solutions because of the formation of an acid which dissolves the manganous sulfid, $Mn^{++} + H_2S \rightleftharpoons MnS + 2H^+$. In solutions alkalin with ammonium hydroxid ammonium sulfid is formed and the precipitation occurs as in 1. In the presence of sodium acetate the precipitate falls, the acetate ion removing the hydrogen ion as undissociated acetic acid.

*3. **Alkali hydroxids** precipitate white manganous hydroxid, $Mn(HO)_2$, insoluble in excess. The precipitate rapidly turns brown absorbing oxygen from the air and becoming hydrated manganic oxid or manganous manganite, $MnMnO_3$, H_2O. This change takes place quickly in the presence of oxidizing agents such as chlorin, bromin and hydrogen peroxid. Ammonium chlorid hinders or prevents the precipitation of manganous hydroxid because of the formation of the soluble ammonium chlormanganite, $(NH_4)_2MnCl_4$, and suppression of hydroxid ion. This compound oxidizes in the air just as the hydroxid does. The solubility of $Mn(HO)_2$ is 0.0055 gram to one liter of water.

4. **Ammonium hydroxid** precipitates incompletely manganous hydroxid. If ammonium chlorid is present there is no precipitation because of the formation of ammonium chlormanganite as in the case of the alkali hydroxids. The solution soon clouds because of oxidation.

5. **Carbonate ions** (Na_2CO_3, K_2CO_3, $(NH_4)_2CO_3$) precipitate white manganous carbonate $MnCO_3$, insoluble in excess, soluble in acids. The precipitate slowly oxidizes in the air to hydrated manganic oxid. The separation is not complete in the presence of ammonium hydroxid.

6. **Sodium phosphate** precipitates white normal manganous phosphate, $Mn_3(PO_4)_2$, soluble in acids. From a hot acid solution of manganous phosphate ammonium hydroxid precipitates white crystallin manganous ammonium phosphate, $MnNH_4PO_4$, $7H_2O$. Compare magnesium.

7. **Lead peroxid** and dilute **nitric acid** (PbO_2 and HNO_3), added to a hot solution containing only traces of manganese, pro-

duce a violet color due to the formation of permanganate ion, MnO_4^-, or permanganic acid, $HMnO_4$. This test (Volhard's) is quite delicate, but does not act in the presence of chlorids or hydrochloric acid or strong nitric acid. The reaction is about as follows:

$$2MnSO_4 + 5PbO_2 + 6HNO_3 = 2PbSO_4 + 3Pb(NO_3)_2 + 2H_2O + 2HMnO_4$$

8. **Potassium cyanid** gives a white precipitate of manganous cyanid, $Mn(CN)_2$, usually brown by oxidation, soluble in excess to a brown solution. From this solution separates green potassium manganous manganocyanid, $K_2MnMnC_6N_6$, which dissolves in further excess of potassium cyanid forming a yellow solution of potassium manganocyanid, $K_4MnC_6N_6$. On dilution the green precipitate reappears. These compounds are oxidized in the air to manganicyanids, $K_3MnC_6N_6$, and both manganocyanid and manganicyanid ions are decomposed by acids with formation of manganous ions. They are also sufficiently unstable to be decomposed by sulfid ion.

9. **Ferrocyanid ion** precipitates white manganous ferrocyanid, $Mn_2FeC_6N_6$, soluble in acids, decomposed by alkalis with separation of the hydroxid.

10. **Ferricyanid ion** precipitates brown manganous ferricyanid, $Mn_3(FeC_6N_6)_2$, difficultly soluble in acids, decomposed by alkalis with separation of the hydroxid.

11. **Dry Reactions.**—*a.* **Bead of borax** is colored by manganese amethyst-red in the oxidizing flame, sodium manganic metaborate, $Na_6Mn_2(BO_2)_{12}$; colorless in the reducing flame, manganous metaborate, $Mn(BO_2)_2$.

b. **Heated on platinum** with alkali hydroxid or carbonate in the presence of an oxidizing agent ($KClO_3$ or KNO_3), alkali manganate is formed, $MnO_2 + Na_2CO_3 = Na_2MnO_4 + CO$. The green mass dissolves in water to a green solution which, on being acidified or warmed or diluted, changes color to pink because of hydrolysis and oxidation to permanganate,

$$3K_2MnO_4 + 2H_2O = 2KMnO_4 + 4KHO + MnO_2.$$

***Determination of the form of Manganese.**—The condition in which the manganese exists in the material under examination can generally be determined by the color of the substance or of its solution.

a. Colorless or pale red darkening when precipitated with ammonium hydroxid:—manganous compounds.

b. Reddish violet, easily reduced and decolorized:—manganic compounds and manganites.

c. Black solid evolving chlorin when heated with hydrochloric acid:—manganese dioxid.

d. Green solid or the solution reddening on exposure to the air:—manganates.

e. Violet or red solution losing color in contact with organic matter:—permanganates.

COBALT

Metallic Cobalt.—Cobalt is iron-white with a tinge of red, has metallic luster, takes a fine polish, is harder than iron and has a specific gravity about 8.7. At 1,200° it absorbs carbon and melts. It tarnishes slightly in moist air and burns when heated to Co_3O_4. It dissolves slowly in most acids, evolving hydrogen; rapidly in nitric acid, liberating oxids of nitrogen.

Cobalt Compounds.—Cobalt forms compounds with most of the negative elements, and yields salts generally with the acids. It is primarily basic but there are a few compounds in which tetravalent cobalt is acidic, as for example, magnesium cobaltate, $MgCoO_3$. It also forms complex compounds with ammonium and cyanogen.

Cobalt Ions.—The elementary positive ions are cobaltous ion, Co^{++}, pink in color and easily oxidized, cobaltic ion, Co^{+++}, green and easily reduced. There are several complex ions usually but slightly colored, cobaltocyanid, $Co(CN)_6^{----}$, cobalticyanid, $Co(CN)_6^{---}$, cobaltothiocyanate, $Co(CNS)_4^{--}$, cobaltous ammonia, $Co(NH_3)_6^{++}$, cobaltic ammonia whose general formula is $Co(NH_3)_n^{+++}$ in which n is 3, 4, 5 or 6.

Cobalt Reactions.—The anhydrous salts of cobalt are blue,

while the hydrous compounds are pink in color. The solution when heated or when very concentrated has the blue color of the anhydrous compound. The sulfate, nitrate and halids are soluble in water.

Use 0.05 N solution of cobalt chlorid, $CoCl_2,6H_2O$, equivalent 118.9, or of cobalt nitrate, $Co(NO_3)_2,6H_2O$, equivalent 145.5.

*1. **Ammonium sulfid** precipitates black cobalt sulfid, CoS, insoluble in excess even in presence of NH_4HO and NH_4Cl and in acetic and dilute hydrochloric acids; soluble in nitric acid, in aqua regia, and in strong hydrochloric acid in presence of potassium chlorate. When it is dissolved in nitric acid or aqua regia the sulfur separates, but by continued action of the acid, is finally oxidized to sulfuric acid. The precipitation is complete in presence of ammonium chlorid (difference from nickel). Cobalt sulfid dissolves in water 0.0038 gram to the liter.

*2. **Hydrogen sulfid** produces no precipitate in acid solutions and only partial precipitation in neutral solutions of cobalt salts. In the presence of alkali acetates the precipitation is complete. Let the student explain. Although not precipitated in acid solution, the precipitate after it is formed is insoluble in hydrochloric acid, and in dilute nitric acid.

*3. **Alkali hydroxids** (NaHO, KHO) precipitate blue basic salts such as CoHOCl, which on boiling are changed to the pink hydroxid, $Co(HO)_2$. If the alkali is concentrated the hydroxid may be precipitated at once. This compound gradually changes in the air to brown cobaltic hydroxid, $Co(HO)_3$, cobalt thus resembling iron and manganese and differing from nickel, which does not oxidize in the air. The change is immediate in the presence of oxidizing agents such as chlorin, bromin, hypochlorite and hydrogen peroxid and is retarded in the presence of nickel hydroxid. Ammonium chlorid hinders the precipitation because of formation of cobalt ammonia salts. Cobalt hydroxid is soluble in acids and in ammonium compounds.

*4. **Ammonium hydroxid** precipitates from neutral solutions the blue basic salt, soluble in ammonium chlorid to a brown solution which contains the complex cobaltous ammonia ion,

$Co(NH_3)_6^{++}$. The latter oxidizes in the air to cobaltic ammonia ions of varying composition. These complex ions are decomposed by alkali hydroxids.

5. **Carbonate ions** (Na_2CO_3, K_2CO_3, $(NH_4)_2CO_3$,) precipitate reddish basic carbonates, soluble in excess of ammonium carbonate or of concentrated potassium carbonate with formation of double salts of uncertain composition, soluble in acids and in ammonium hydroxid.

6. **Phosphate ions** precipitate pink cobalt phosphate, $Co_3(PO_4)_2$, soluble in dilute acids even acetic and in ammonium hydroxid.

*7. **Potassium nitrite,** KNO_2, precipitates from strong acetic acid solutions of cobalt salts, yellow potassium cobaltinitrite, $K_3Co(NO_2)_6$. If the solution is dilute the separation takes place slowly. This is a good reaction for the detection of cobalt in nickel salts.

*8. **Potassium cyanid** precipitates from neutral solutions brown cobalt cyanid, $Co(CN)_2$, soluble in excess to a brown solution containing cobaltocyanid ion, $Co(CN)_6^{----}$, easily oxidized to cobalticyanid, $Co(CN)_6^{---}$. The oxidation of cobaltocyanid to cobalticyanid serves to separate cobalt from nickel. Cobalt cyanid is soluble in acids and in ammonium hydroxid and is decomposed by alkali hydroxids.

9. **Ammonium thiocyanate,** NH_4CNS, (Vogel's reaction) added to a cobaltous solution, produces a beautiful blue color, due to the formation of ammonium cobaltothiocyanate, $(NH_4)_2Co(CNS)_4$. On adding water the blue color changes to pink. If now amyl alcohol, or a mixture of amyl alcohol and ether is added, and the mixture shaken, the alcohol is colored blue. The test is very delicate. Nickel does not color amyl alcohol. If iron is present red ferric thiocyanate is formed and masks the blue color. The addition of a little sodium carbonate precipitates the iron as ferric hydroxid and the blue color of the cobalt reappears.

10. **Ferrocyanid ion** precipitates drab colored cobalt ferrocyanid, $Co_2FeC_6N_6$, insoluble in dilute acids, soluble in ammonium hydroxid, and in concentrated mineral acids.

11. **Ferricyanid ion** precipitates red cobalt ferricyanid, $Co_3(FeC_6N_6)_2$, insoluble in dilute acids and in ammonium hydroxid, soluble with difficulty in concentrated acids.

12. **Dry Reactions.**—Borax bead gives in either oxidizing or reducing flame a blue coloration of sodium cobalt metaborate, $Na_2Co(BO_2)_4$. Many metallic oxids give colored beads which are decolorized more or less in the reducing flame.

NICKEL

Metallic Nickel.—Nickel is a silver-white, malleable, ductile metal of specific gravity 8.9 and melting point above 1,500°. It tarnishes slowly in moist air and burns when heated to nickel oxid, Ni_2O_3. It dissolves slowly in dilute acids evolving hydrogen. With strong sulfuric and nitric acids it acts like copper yielding when heated with them in the first case sulfurous oxid, SO_2, and in the second case nitrogen dioxid, N_2O_2. It forms alloys with other metals the most important of which are German silver (Cu 5, Ni 2, Zn 2) and nickel coin (Ni 1, Cu 3).

Nickel Compounds.—Nickel compounds are similar to those of iron and cobalt. Nickel has scarcely a trace of negative quality and forms neither acid nor nickelate. There are, however, a few cyannickelates. The valence is two, rarely three. The nickelic compounds are easily reduced.

Nickel Ion.—Nickel forms one elemental ion, N^{++}, green in color, basic and poisonous. There are complex ammonia ions and cyannickelate ions similar to those of cobalt.

Nickel Reactions.—Of the common salts of nickel the nitrate, sulfate and halids are soluble in water.

Use 0.05 N solution of nickel chlorid, $NiCl_2$, $6H_2O$, equivalent 118.8; or of nickel sulfate, $NiSO_4$, $7H_2O$, equivalent 140.3.

*1. **Ammonium sulfid** precipitates from neutral solutions black nickel sulfid, NiS, soluble in large excess in the presence of ammonium hydroxid, nickel ammonia sulfid, $Ni(NH_3)_6S$, being formed. The precipitate is reformed on adding acetic acid and boiling. Ammonium salts prevent the solution of the precipitate

by driving back the dissociation of NH_4HO. Nickel sulfid is almost insoluble in dilute acids, soluble in nitric acid or aqua regia, and in hydrochloric acid with a crystal of potassium chlorate, scarcely soluble in sulfuric acid, soluble in water 0.0036 gram to the liter. Nickel sulfid runs through the filter badly, a trouble which may be prevented by boiling the precipitate with ammonium acetate.

*2. **Hydrogen sulfid** produces no precipitate in acid solutions and only partial precipitation in neutral solutions because of separation of hydrogen ion. In presence of alkali acetate the precipitation of nickel sulfid is complete because the excess of acetate ion drives the hydrogen ion back into combination as undissociated acetic acid.

*3. **Alkali hydroxids** (NaHO, KHO) precipitate green nickel hydroxid, $Ni(HO)_2$ insoluble in excess, soluble in acids and in ammonium salts. It is unchanged in the air but is converted by oxidizing agents (bromin water) into black nickelic hydroxid, $Ni(HO)_3$.

*4. **Ammonium hydroxid** in neutral solutions free from ammonium ions precipitates a green basic salt ($NiHO^+$) soluble in excess of the reagent to a bluish green solution which contains nickel ammonia ions, $Ni(NH_3)_6^{++}$. In the presence of ammonium chlorid, the halosalt ammonium chlornickelate, $(NH_4)_2NiCl_4$, is formed, but with excess of ammonium hydroxid the reaction is reversed and the nickel ammonia ions are reformed.

5. **Alkali carbonates** (Na_2CO_3, K_2CO_3) precipitate pale green nickel carbonate more or less basic soluble in strong potassium carbonate and reprecipitated on dilution, soluble in acids and in ammonium hydroxid, insoluble in alkalis.

6. **Ammonium carbonate** in neutral solutions precipitates nickel carbonate, $NiCO_3$, soluble in excess to bluish nickel ammonia carbonate, $Ni(NH_3)_6CO_3$.

7. **Sodium phosphate** precipitates pale green nickel phosphate, $Ni_3(PO_4)_2$, soluble in ammonium hydroxid and in acids, even acetic.

8. **Potassium nitrite** gives no precipitate with dilute solutions (difference from cobalt). In concentrated solutions a brown precipitate of potassium nickelonitrite, $K_4Ni(NO_2)_6$, falls. Note that cobalt forms the cobaltinitrite. In presence of alkali earth ions a yellow crystallin precipitate is formed; as for example, potassium barium nickelonitrite, $K_2BaNi(NO_2)_6$.

*9. **Potassium cyanid** precipitates green nickel cyanid, $Ni(CN)_2$, soluble in excess to potassium cyannickelate, $K_2Ni(CN)_4$, which is decomposed by dilute acids, nickel cyanid being precipitated and hydrogen cyanid being evolved. It is not decomposed by ammonium sulfid but yields readily to oxidizing agents giving finally nickelic hydroxid. This reaction furnishes a delicate test for nickel in presence of cobalt. It may be brought about as follows: To a few drops of the solution, neutralized with sodium carbonate if necessary, add potassium cyanid to a clear solution avoiding excess, then add a little alkali hydroxid and pass chlorin gas or add bromin water. Nickelic hydroxid, $Ni(HO)_3$, will fall in a few minutes.

10. **Ferrocyanid ion** precipitates pale green nickel ferrocyanid, $Ni_2FeC_6N_6$, soluble in ammonium hydroxid, insoluble in dilute acids, soluble in concentrated HCl.

11. **Ferricyanid ion** precipitates brown nickel ferricyanid, $Ni_3(FeC_6N_6)_2$, insoluble in dilute acids, soluble in ammonium hydroxid (difference from cobalt).

12. **Dry Reactions.**—Borax bead takes in the oxidizing flame the brown or yellow color of sodium nickel metaborate, $Na_2Ni(BO_2)_4$, and in the reducing flame the gray color of metallic nickel.

Analysis of the Zinc Group

SEPARATION AND IDENTIFICATION OF THE METALS AND IONS OF GROUP 4

Metals other than those of Groups 1, 2 and 3, whose sulfids are insoluble in alkalis.

Metals: Zinc, manganese, cobalt, nickel.

Ions: Zn^{++}, Mn^{++}, Co^{++}, Ni^{++}.

Group reagent: Ammonium sulfid with ammonium hydroxid and ammonium chlorid.

Principle.—The ions of this group unite to the sulfid ion to form molecular sulfids which are insoluble in water and in alkalis. Since these sulfids are soluble in acids the solution must be kept alkalin. This is best done by using ammonium sulfid as the precipitant in the presence of ammonium hydroxid. The precipitation of the hydroxids of the metals is prevented by ammonium chlorid as in Group 2.

Group Reagent.—Any soluble sulfid will serve as the reagent for this group. Ammonium sulfid is best, since the solution already contains the ammonium ion which can be expelled at any time by boiling with alkali hydroxid or by evaporation and ignition. Ammonium hydroxid is used to keep the solution alkalin and ammonium chlorid to prevent the precipitation of the hydroxids.

The Precipitate.—The precipitate may be white zinc sulfid, ZnS, pink manganese sulfid, MnS, black cobalt sulfid, CoS, black nickel sulfid, NiS. Because of the reducing action of the reagent cobaltic and manganic compounds do not appear in the precipitate.

Preparation of the Solution.—The ammoniacal filtrate from Group 3 will generally need no special preparation. It should be decidedly alkalin and to insure this a few drops of ammonium hydroxid may be added. If a precipitate forms, it will be dissolved by adding a little ammonium chlorid. If the solution is very dilute, it should be concentrated by boiling and then made alkalin with ammonium hydroxid.

In precipitating the metals of this group we may boil the solution to expel ammonia and then add the group reagent ammonium sulfid. In this case the sulfids separate in the colloidal state and are apt to run through the filter. It is better, therefore, to pass hydrogen sulfid through the ammoniacal liquid. The hydrogen sulfid and the ammonium hydroxid unite to form the group reagent and the precipitate is less colloidal. If it still runs through the filter, warm it and add a little ammonium acetate. It sometimes happens that a little of Group 2 passes over into the solution used for this group. To ascertain if such

is the case, acidify a small portion with hydrochloric acid and pass hydrogen sulfid. If a precipitate falls, treat the whole solution in the same way, filter and make the filtrate alkalin with ammonium hydroxid.

The Analysis.—1. Pass hydrogen sulfid through the solution prepared as above until no more precipitate forms. Warm gently, or boil off excess of ammonia if necessary, filter and wash thoroughly with water containing hydrogen sulfid. Reject the washings. Manganese sulfid forms slowly and so the filtrate may contain some manganese ion. It soon falls, however, and the filtration may be repeated. If the precipitate is white, only zinc can be present; if it is pink, manganese is indicated and possibly zinc; if it is black, all may be present. If the filtrate runs through brown, nickel is present and is incompletely removed. In this case add a little acetic acid to the filtrate, being careful to let it remain alkalin, and warm for a few minutes. Ammonium acetate is formed and causes the coagulation of the precipitate. Pour through the filter again.

The filtrate contains the ions of Groups 5 and 6.

The precipitate may consist of ZnS, MnS, CoS, NiS.

2. Treat the precipitate of 1 on the filter with a few cubic centimeters of dilute hydrochloric acid of normal strength through which a little H_2S has been passed, pouring the acid over it several times. The sulfids of zinc and manganese dissolve as chlorids and those of cobalt and nickel remain on the filter. Wash with water containing hydrogen sulfid to prevent oxidation, rejecting the wash water.

The filtrate contains zinc and manganese ions along with chlorid ions.

The residue consists of cobalt and nickel sulfids.

3. Boil the filtrate of 2 to expel ammonium sulfid and add alkali hydroxid in excess. White zinc hydroxid, $Zn(HO)_2$, precipitates, but immediately dissolves to alkali zincate, Na_2ZnO_2, or K_2ZnO_2; and also white manganous hydroxid, $Mn(HO)_2$, which rapidly oxidizes in the air to brown manganic hydroxid, $Mn(HO)_3$. Filter and wash.

The filtrate contains sodium or potassium zincate, Na_2ZnO_2.

The precipitate is $Mn(HO)_2$ and $Mn(HO)_3$.

4. Pass hydrogen sulfid through the filtrate of 3. A white precipitate of zinc sulfid indicates the presence of zinc. The precipitate is often indistinct, but is rendered visible by boiling. It may be dark-colored because of the presence of iron sulfid, the iron having been imperfectly separated in Group 3. This color is removed by careful addition of acetic acid, the iron sulfid going into solution while the zinc sulfid remains. If the latter also dissolves, it may be reprecipitated by adding hydrogen sulfid. Care must be taken not to mistake for zinc sulfid the precipitate of sulfur which generally separates when acids are added to ammonium sulfid solutions. Zinc sulfid is flocculent, while sulfur is milky. The precipitation of the iron may be prevented by adding a few drops of KCN before passing the H_2S.

5. The change of color of the precipitate of 3 from white to brown is generally sufficient evidence of the presence of manganese. To confirm transfer a portion to platinum foil and fuse with sodium carbonate and potassium nitrate. A green manganate turning to red when moistened with acetic acid indicates manganese.

6. Test with borax beat the residue of 2, heating strongly in the reducing flame. Blue indicates cobalt; brown or yellow in the outer flame, gray or opaque in the inner flame, indicates nickel. If the color is intermediate, both metals may be present. With either metal alone, the test is generally satisfactory; when both are present, further examination is needed.

7. If the borax test has not given conclusive evidence, proceed as follows: Dissolve the residue of 2 on the filter with one or two cubic centimeters of hot strong nitric acid, receiving the filtrate in a porcelain dish and pouring the acid through two or three times if necessary. The separated sulfur will remain on the filter. Evaporate the solution carefully to dryness, avoiding overheating. Dissolve the residue in 10 cc. of water, divide in three portions and treat in one or more of the following ways:

a. To the first portion in a test-tube add an equal quantity of sodium hydroxid solution and mix thoroughly. A blue precipitate changing at once to pink means cobalt alone. A pale green precipitate remaining unchanged means nickel alone. Blue changing slowly to pink indicates much cobalt with little nickel. Green with more or less bluish tint indicates much nickel and little cobalt. This test is quite delicate and retardation of the change from blue to pink may be brought about even by the traces of nickel which are usually found in the cobalt salts of the laboratory (Benedict Method). See American Chemical Journal, 26, 695, 1904.

b. To the second portion of the solution add potassium cyanid (fresh solution) until the precipitate just dissolves and boil. Add sodium hydroxid in excess and then bromin water until the color of the bromin persists. A black precipitate is nickelic hydroxid $Ni(HO)_3$. The solution contains sodium cobalticyanid, $Na_3CoC_6N_6$, and may be tested with borax bead for cobalt.

c. To the third portion of the solution add sodium hydroxid or sodium carbonate until the precipitate is just permanent, add acetic acid in slight excess, then sodium acetate, and finally an excess of a fresh concentrated solution of potassium nitrate. If cobalt is present a yellow crystalline precipitate falls of potassium cobaltinitrite, $K_3CO(NO_2)_6$. Let stand for several hours, then filter and add sodium hydroxid to the filtrate. A precipitate of green nickel hydroxid $Ni(HO)_2$ indicates nickel.

TABLE FOR GROUP 4

Metals: Zinc, manganese, cobalt, nickel.

Ions: Zn^{++}, Mn^{++}, CO^{++}, Ni^{++}.

Group reagent: Ammonium sulfid with NH_4HO and NH_4Cl. Prepare the solution and make the precipitations as directed above.

Filtrate contains ions of Groups 5 and 6.

Precipitate is ZnS, MnS, CoS, NiS.

Treat the precipitate on the filter with normal HCl through which a little H_2S has been passed and wash with water containing H_2S, rejecting the washings.

<table>
<tr><td colspan="2">Filtrate contains zinc and manganese ions along with chlorid ions. Boil to expel $(NH_4)_2S$ and add NaHO in excess.</td><td>Residue is CoS and NiS. Treat with borax bead. Dissolve on filter with hot strong HNO_3, evaporate to dryness, or boil off excess of acid, dissolve in water and divide in three portions.</td></tr>
<tr><td rowspan="5">Filtrate contains ZnO_2-- or Na_2ZnO_2. Pass H_2S. White ZnS indicates zinc.</td><td rowspan="5">Precipitate is $Mn(HO)_2$ and $Mn(HO)_3$. Fuse with Na_2CO_3 and KNO_3. Green manganate indicates manganese.</td><td>a. Add NaHO and mix. Interpret colors as explained in 7 a above.</td></tr>
<tr><td>b. Add KCN, NaHO and Br as directed in 7 b.</td></tr>
<tr><td>Solution contains $Na_3CoC_6N_6$. Test with borax bead.</td></tr>
<tr><td>Precipitate is black $Ni(HO)_3$. Test with borax bead.</td></tr>
<tr><td>c. Add NaHO just to excess, $HC_2H_3O_2$ to excess, $NaC_2H_3O_2$, and KNO_2 to excess.</td></tr>
<tr><td></td><td>Precipitate is $K_3Co(NO_2)_6$. Test with borax bead. Blue indicates cobalt.</td><td>Filtrate contains $Ni(C_2H_3O_2)_2$. Add NaHO. Precipitate is green $Ni(HO)_2$, indicating nickel.</td></tr>
</table>

Chapter X

GROUP 5. BARIUM GROUP

Barium, Strontium, Calcium

Properties and Reactions of the Metals and Ions of Group 5

BARIUM

Metallic Barium.—Barium is a yellow solid which melts at red heat and has specific gravity 3.6. It tarnishes in the air, decomposes water and dissolves in acids. Its characteristic compound is the insoluble sulfate, $BaSO_4$.

Barium Compounds.—Barium unites to many of the negative elements and forms salts with most of the acids. Its valence is two except in a few compounds. It is active and most of its salts are soluble in water.

Barium Ion.—Barium forms one elemental positive ion, Ba^{++}, which is colorless, active and poisonous. It forms no complex ions and no anion with oxygen. It is, therefore, wholly positive and basic.

Reactions of Barium Ion.—Soluble compounds of barium are halids, nitrate, chlorate, acetate and sulfid. Use for the reactions 0.05 N solution of the nitrate, $Ba(NO_3)_2$, equivalent 130.8; or of the chlorid, $BaCl_2$, $2H_2O$, equivalent 122.6.

*1. **Ammonium carbonate** precipitates white amorphous barium carbonate, $BaCO_3$, insoluble in alkali and ammonium hydroxids, soluble in acids (except sulfuric which makes insoluble barium sulfate), and in hydrogen ammonium carbonate because of formation of the soluble acid carbonate. Since ammonium carbonate easily decomposes into NH_3 and HNH_4CO_3, it is necessary to prevent this decomposition by adding ammonium hydroxid before using the reagent. Barium carbonate is slightly soluble in ammonium chlorid as is explained on page 143. It dissolves in water 0.024 gram to the liter.

2. **Alkali carbonate** acts like ammonium carbonate.

3. **Ammonium hydroxid** gives no precipitate except in concentrated solutions because barium hydroxid, $Ba(HO)_2$ is rather soluble in water, about 37 grams to the liter. When the mixture is exposed to the air, barium carbonate is formed by absorption of carbon dioxid. Alkali hydroxids act in the same way.

*4. **Sulfate ion** precipitates white, finely divided barium sulfate, $BaSO_4$, practically insoluble in water, acids and alkalis, slightly soluble in hot concentrated acids, insoluble in strong solution of ammonium sulfate (difference from calcium). One liter of water dissolves 0.0025 gram $BaSO_4$.

*5. **Chromate ion** (soluble chromates) precipitate yellow barium chromate, $BaCrO_4$, soluble in mineral acids but not in acetic acid, insoluble in alkalis. It is almost insoluble in water, 0.0038 gram to the liter, thus differing from strontium chromate which is moderately soluble and calcium chromate which is quite soluble. It is converted by boiling potassium carbonate solution into barium carbonate.

$$BaCrO_4 + K_2CO_3 = BaCO_3 + K_2CrO_4.$$

Dichromate ion gives the same precipitate.

6. **Sodium phosphate,** Na_2HPO_4, precipitates white barium phosphate, $Ba_3(PO_4)_2$, from alkalin, and barium hydrogen phosphate, $BaHPO_4$, from neutral, solutions, both soluble in acids even acetic, insoluble in alkalis. See under phosphate ions.

7. **Fluosilicic acid** precipitates white barium fluosilicate, $BaSiF_6$, difficultly soluble in alcohol (difference from strontium and calcium fluosilicates which are readily soluble in water and in alcohol).

*8. **Ammonium oxalate** precipitates white barium oxalate, BaC_2O_4, insoluble in alkalis, soluble in strong acids, in boiling acetic acid, and in water 0.09 gram to the liter.

*9. **Concentrated acids** (HCl and HNO_3) precipitate the corresponding salts ($BaCl_2$ and $Ba(NO_3)_2$). See mass law.

*10. **Sodium sulfite,** Na_2SO_3, precipitates white barium sulfite, $BaSO_3$, insoluble in alkalis, and in dilute acids, soluble in concentrated acids, and in water 0.01 gram to the liter.

11. **Dry Reactions.**—*a.* Heated on platinum wire in the Bunsen flame barium salts give an apple-green color.

b. The spectrum consists of several lines, some in the orange and some in the green.

STRONTIUM

Metallic Strontium.—Strontium is a yellow metal with specific gravity 2.5 and melting-point 700°. It decomposes water, dissolves in acids, burns in air, in oxygen, in carbon dioxid and in vapors of bromin, iodin and sulfur.

Strontium Compounds.—Strontium is quite active and yields numerous compounds. It unites with the negative elements generally and forms salts with the acids. Its usual valence is two, but it is tetravalent in peroxids and persulfids. The electric quality is wholly positive and the oxids have no acid properties.

Strontium Ion.—Strontium forms one colorless elemental ion, Sr^{++}, but no complex ions.

Strontium Reactions.—The halids, nitrate, acetate and sulfid of strontium are soluble in water. The nitrate is insoluble in alcohol (difference from calcium). Use 0.05 N solution of the nitrate, $Sr(NO_3)_2{,}4H_2O$, equivalent 141.8; or of the chlorid, $SrCl_2$, $6H_2O$, equivalent 133.

*1. **Carbonate ions** (Na_2CO_3, K_2CO_3, $(NH_4)_2CO_3$) precipitate strontium carbonate, $SrCO_3$ practically insoluble in water, in alkalis and in ammonium hydroxids, soluble in acids, more soluble than barium carbonate in ammonium chlorid. It dissolves in water 0.01 gram to the liter.

*2. **Sulfate ions** (soluble sulfates) precipitate white strontium sulfate, more soluble in water than barium sulfate but less so than calcium sulfate, soluble in acids, insoluble in ammonium sulfate (difference from calcium), in ammonium hydroxid and in alkalis. It dissolves in water 0.114 gram to the liter at 18°.

*3. **Ammonium oxalate** precipitates white strontium oxalate, SrC_2O_4, insoluble in water, alkalis and ammonium hydroxid, soluble in acids except acetic, which dissolves it slightly. Its solubility in water is 0.045 gram to the liter at 18°.

4. **Chromate ions** precipitate from concentrated solutions, yellow $SrCrO_4$, soluble in water and in acids, even acetic.

*5. **Sodium Sulfite,** Na_2SO_3, precipitates white strontium sulfite, $SrSO_3$, almost insoluble in dilute acids, especially acetic, soluble in concentrated acids except acetic, in water 0.033 gram to the liter.

*6. **Dry Reactions.**—*a.* Heated in the Bunsen flame the volatile salts of strontium give a characteristic crimson color.

b. The spectrum of strontium contains several lines in the red and one in the blue.

CALCIUM

Metallic Calcium.—Calcium is a white, lustrous, crystallin, ductile, malleable solid of specific gravity 1.58 and with boiling-point 760°. The commercial article has a brass yellow color. It tarnishes in the air and burns, uniting to both the oxygen and the nitrogen. It dissolves in acids but not in alkalis.

Calcium Compounds.—Calcium is active, uniting to the negative elements and forming salts with the acids. It is bivalent and wholly positive.

Calcium Ion.—Calcium forms one elemental kation, $Ca++$, colorless, bivalent and strongly positive, which holds its electric charge firmly and does not give it readily to other elements.

Calcium Reactions.—The salts of calcium are somewhat more soluble than those of barium and strontium. Some of them, such as the chlorid and nitrate, are quite deliquescent. The sulfate even is rather soluble in water, 2.2 grams to the liter. The oxalate, however, is less soluble than the oxalates of barium and strontium. The nitrate is soluble in alcohol (difference from strontium).

Use 0.05 N solution of calcium nitrate, $Ca(NO_3)_2{,}4H_2O$, equivalent 118; or of calcium chlorid, $CaCl_2$, equivalent 55.5.

*1. **Carbonate ions** (Na_2CO_3, K_2CO_3, $(NH_4)_2CO_3$) precipitate white amorphous calcium carbonate, $CaCO_3$, which on warming gradually becomes crystallin (calcite). Calcium carbonate dissolves in all acids with effervescence, but not in alkalis. It dissolves in water 0.013 gram to the liter, and in water containing

carbon dioxid it passes into solution as calcium hydrogen carbonate, $CaH_2(CO_3)_2$ about one gram to the liter. On evaporating the solution the acid carbonate is decomposed and the normal carbonate is precipitated. It dissolves in the presence of much ammonium chlorid, calcium chlorid being formed by metathesis.

$$CaCO_3 + 2NH_4Cl \rightleftharpoons (NH_4)_2CO_3 + CaCl_2.$$

When the mixture is boiled the ammonium carbonate decomposes into ammonia, carbon dioxid and water, and the reaction continues until the calcium carbonate is all dissolved.

2. **Ammonium hydroxid** produces no precipitate in calcium solutions. Alkali hydroxids precipitate calcium hydroxid in concentrations above 1.16 grams to the liter.

*3. **Ammonium oxalate** precipitates from neutral or alkalin solutions white finely crystallin calcium oxalate, CaC_2O_4, practically insoluble in water and acetic acid, but readily soluble in strong acids. It dissolves in water 0.006 gram to the liter at 20°. It is converted by sulfuric acid into calcium sulfate and by boiling solution of sodium carbonate into calcium carbonate. When precipitated from hot solutions the crystals of calcium oxalate are larger and filter better.

*4. **Sulfate ions** precipitate from concentrated solutions white calcium sulfate, $CaSO_4$, insoluble in alcohol, soluble in acids, and in water 2 grams to the liter. It is converted by boiling sodium carbonate into calcium carbonate because of the smaller solubility of this compound.

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4.$$

5. **Sodium phosphate,** Na_2HPO_4, precipitates from ammoniacal solutions calcium phosphate, $Ca_3(PO_4)_2$, insoluble in alkalis, readily soluble in acids even acetic, soluble in water 0.025 gram to the liter. In neutral solutions the precipitate is acid calcium phosphate, $CaHPO_4$.

6. **Potassium ferrocyanid** precipitates from alkalin solutions pale yellowish green potassium calcium ferrocyanid, $K_2CaFe(CN)_6$, insoluble in excess, soluble in acids. Strontium

solutions and dilute barium solutions yield no precipitate with ferrocyanid ion.

*7. **Sodium sulfite,** NA_2SO_3, precipitates white $CaSO_3$ scarcely soluble in ammonium and alkali hydroxids, soluble in acids even acetic, and in water 1.2 gram to the liter.

8. **Potassium ferricyanid** gives a pale green precipitate of potassium calcium ferricyanid, $KCaFe(CN)_6$, soluble in acids.

9. **Dry Reactions.**—*a.* Heated on platinum wire calcium compounds give to the non-luminous flame a brick-red color. With sodium carbonate on charcoal they are reduced to white infusible calcium oxid.

b. The spectrum of calcium contains lines in the orange, yellow, green and violet. The green and orange lines are prominent on either side of the sodium line.

Analysis of the Barium Group

SEPARATION AND IDENTIFICATION OF THE METALS AND IONS OF GROUP 5

Metals, other than those of Groups 1, 2, 3 and 4, whose carbonates are insoluble in alkalin solutions.

Metals: Barium, strontium, calcium.

Ions: Ba^{++}, Sr^{++}, Ca^{++}.

Group reagent: Ammonium carbonate with ammonium hydroxid and ammonium chlorid.

Principle.—The ions of this group combine with carbonate ions to form molecular carbonates, which are insoluble in dilute ammonium hydroxid even in the presence of ammonium chlorid. They will, therefore, be precipitated by soluble carbonates. Ammonium chlorid prevents the precipitation of magnesium ion, but must not be present in too great excess, since it exerts some solvent action on the carbonates of this group. Ammonium hydroxid prevents the formation of hydrogen ammonium carbonates in which the carbonates are soluble.

Group Reagent.—Any soluble carbonate will serve as reagent for the group. Ammonium carbonate is used because the ammonium ions help to make the precipitation complete by diminish-

ing the dissociation of ammonium chlorid and thereby inhibiting its solvent action. The solid ammonium carbonate consists mainly of hydrogen ammonium carbonate, HNH_4CO_3, and ammonium carbamate, $NH_4NH_2CO_2$, which are both converted by ammonium hydroxid into normal ammonium carbonate.

The Precipitate.—The precipitate may be barium carbonate, $BaCO_3$ strontium carbonate, $SrCO_3$, calcium carbonate, $CaCO_3$, all white. Magnesium is held in solution by the ammonium chlorid, the excess of ammonium ion so reducing the dissociation of ammonium carbonate that the concentration of magnesium carbonate does not exceed its solubility.

The precipitation is aided by heat, but boiling causes decomposition of the carbonates with escape of ammonia and carbon dioxid:

$$(NH_4)_2CO_3 = 2NH_3 + H_2O + CO_2.$$

The concentration of the carbonate ions is thus so reduced that the precipitate passes back into solution An excess of ammonium salts has a similar effect:

$$BaCO_3 + 2NH_4Cl = BaCl_2 + CO_2 + 2NH_3 + H_2O.$$

If, therefore, ammonium chlorid is present in considerable excess of the quality necessary to keep magnesium in solution, having been formed or added in the process of separating the previous groups, it should be removed by evaporation and gentle ignition. The dry residue is dissolved in water with a little hydrochloric acid and then made alkalin with ammonium hydroxid. If a precipitate of magnesium falls, dissolve it with just enough ammonium chlorid, or filter off the excess.

Preparation of the Solution.—The filtrate from Group 4 is boiled with a few drops of acetic acid until ammonium sulfid is completely decomposed and the hydrogen sulfid and ammonia are expelled. The ammonium and sulfid ions react with water to form hydrogen sulfid and ammonium hydroxid,

$$2NH_4^+ + S^{--} + 2H_2O = 2NH_4OH + H_2S.$$

The ammonium hydroxid decomposes into ammonia and water

and the hydrogen sulfid and ammonia are driven off as gases. If yellow ammonium sulfid is present, hydrogen polysulfid, H_2S_n, is formed from which sulfur separates at the boiling temperature. This sulfur may be removed by filtration. The acetic acid hastens the decomposition of the ammonium sulfid. If the solution contains too large a quantity of ammonium salts, the excess must be expelled by evaporation and gentle ignition in porcelain. This is because the compounds of this group are slightly soluble in concentrated solutions of ammonium salts. On the contrary, there must be enough present to hold the magnesium in solution.

The Analysis.—1. The solution as prepared above, or the filtrate from some previous group, is made alkalin with ammonium hydroxid and heated nearly to boiling. If a precipitate of magnesium hydroxid falls, ammonium chlorid is added until it dissolves. Ammonium carbonate is then added with constant stirring until no more precipitate forms. The mixture should be heated, but not boiled for reasons already explained. Filter and wash with hot water.

If the solution is very dilute and much ammonium chlorid is present, there may be no precipitate, although the ions of the group may be present. In this case, test a small portion with sulfate ion for barium and strontium and another portion with oxalate ion for calcium.

The filtrate contains the ions of Group 6.

The precipitate is $BaCO_3$, $SrCO_3$, $CaCO_3$.

2. Dissolve the precipitate of 1 in a very small quantity of warm dilute acetic acid. To a portion of the solution add potassium dichromate, and a little sodium acetate to diminish the solvent action of the acetic acid. A yellow precipitate of $BaCrO_4$ indicates the presence of barium. If there is no precipitate, barium is absent, and the remainder of the solution need not be treated with the dichromate. If there is a precipitate, add to the whole solution enough dichromate to remove all the barium, filter and wash.

Filtrate contains calcium, strontium, acetate and dichromate ions.

Precipitate is barium chromate, $BaCrO_4$.

3. Boil the precipitate of 2 with potassium carbonate, converting barium chromate into barium carbonate, filter, wash free from chromate ion, dissolve in hydrochloric acid and add sulfate ion. White $BaSO_4$ insoluble in hydrochloric acid confirms barium.

4. Make the yellow filtrate of 2 alkalin with ammonium hydroxid, add ammonium carbonate to reprecipitate the carbonates of strontium and calcium, filter, wash free from chromate ion and dissolve on the filter with the least quantity of acetic acid. If no barium was found, omit this process and use the acetic acid solution of 2.

5. To a portion of the solution of 4 (or of 2 if barium is absent) add a saturated solution of calcium sulfate, heat to boiling and set aside. A slowly forming precipitate is strontium sulfate, $SrSO_4$. Filter, wash, dissolve in hydrochloric acid and transfer with platinum wire to Bunsen flame. Crimson color confirms strontium.

6. To another portion of the solution of 4 (or of 2 if barium is absent) add potassium or ammonium sulfate, warm and filter. Strontium and calcium sulfates are both precipitated up to the limits of their solubility, 0.114 gram to the liter for the former and 2 grams for the latter. The filtrate will, therefore, be practically free from strontium, but will contain most of the calcium. To the filtrate add ammonium oxalate. White calcium oxalate, CaC_2O_4, insoluble in acetic acid, soluble in hydrochloric acid, confirms calcium. If strontium was found, the filtrate should be diluted to two and a half times its volume to bring the concentration of the strontium oxalate below the limit of its solubility, 0.046 gram to the liter.

7. As an alternative method for calcium and strontium, free the filtrate of 2 from chromate ion as in 4, dissolve the precipitate in a little nitric acid, evaporate nearly to dryness, add 10 cc. amyl alcohol and boil the mixture half away. (Use care

since the vapor is inflammable.) Filter and wash with absolute alcohol.

Precipitate is $Sr(NO_3)_2$.

Filtrate contains calcium and nitrate ions.

a. Test precipitate for strontium with flame or spectroscope.

b. Add to the filtrate an equal volume of common alcohol and a few drops of dilute sulfuric acid. White precipitate is $CaSO_4$.

9. **Sulfite Method for Strontium and Calcium.**—Calcium sulfite is quite soluble in acetic acid while strontium sulfite dissolves with difficulty. This fact furnishes a means of easy, rapid and accurate separation of calcium and strontium.* The process is carried out as follows:

8. To 10 cc. of the solution of 4 add 5 cc. of a freshly prepared concentrated solution of sodium sulfite. A precipitate may be $SrSO_3$ or $CaSO_3$ or both. Add 2 cc. of acetic acid, heat to boiling, filter and wash.

The filtrate contains calcium ions.

The undissolved residue is $SrSO_3$.

9. Dilute the filtrate slightly and add ammonium oxalate. A white precipitate is CaC_2O_4.

10. Dissolve the residue of 8 in HCl and test the solution with platinum wire in Bunsen flame for strontium. If the quantity of strontium present is small, the color may be masked by calcium which may not have been completely removed. In this case, use two wires, dipping one in the solution under examination and the other in a pure HCl calcium solution. Bring them into the flame on opposite sides and compare the colors after the sodium and potassium have burned away. Even a trace of strontium may be thus detected in the presence of calcium.

TABLE FOR GROUP 5

Metals: Barium, strontium, calcium.

Ions: Ba^{++}, Sr^{++}, Ca^{++}.

Group reagent: Ammonium carbonate with NH_4OH and NH_4Cl.

Prepare the solution as directed, add NH_4OH to alkalin reaction and enough NH_4Cl to keep magnesium in solution, then

* See Hinds in *Journal of American Chemical Society*, 33, 510.

add ammonium carbonate till precipitation is complete, warm gently, filter, wash.

Filtrate contains the ions of Group 6.

Precipitate is $BaCO_3$, $SrCO_3$, $CaCO_3$.

Dissolve the precipitate in a small quantity of warm dilute acetic acid and to a portion of the solution add $K_2Cr_2O_7$. If there is no precipitate, barium is absent and the remainder of the solution is examined for strontium and calcium. If there is a yellow precipitate, indicating barium, treat the whole solution with just enough of the dichromate to remove the barium, filter and wash.

The filtrate contains strontium and calcium ions, along with dichromate, acetate and hydrogen ions.

The precipitate is yellow barium chromate, $BaCrO_4$.

Boil the precipitate with K_2CO_3, filter, wash, dissolve the $BaCO_3$ in HCl and add sulfate ion. White $BaSO_4$ confirms barium.

Make filtrate alkalin with NH_4OH, add $(NH_4)_2CO_3$, filter, wash clear of chromate ion. Divide in two portions.

a. Dissolve one portion in acetic acid.

To a portion of the solution add $CaSO_4$, warm, filter, wash. Precipitate is $SrSO_4$ indicating **strontium**. Confirm by flame reaction.	To another portion add K_2SO_4, boil, filter. To the filtrate add $(NH_4)_2C_2O_4$. White CaC_2O_4 insoluble in acetic acid, soluble HCl confirms **calcium**.

b. Dissolve the other portion in nitric acid, evaporate nearly to dryness, add 10 cc. amyl alcohol, boil half away, filter, wash with absolute alcohol.

Precipitate is $Sr(NO_3)_2$ indicating **strontium**. Confirm with flame reaction or spectroscope.	Add to filtrate equal volume of common alcohol and a few drops of H_2SO_4. White $CaSo_4$ confirms **calcium**.

c. To a portion of the acetic acid solution (a) add Na_2SO_3, then acetic acid, boil and filter.

To the filtrate add $(NH_4)_2C_2O_4$. White CaC_2O_4 confirms **calcium**.	Dissolve the residue in HCl and test solution in flame for **strontium**. See 10 above.

Chapter XI

GROUP 6. MAGNESIUM-ALKALI GROUP

Magnesium, Sodium, Potassium, Lithium, Ammonium, Hydrogen

This is a mixed group and contains those kations which remain in the solution after the members of the other groups have been removed, as well as ammonium ion and hydrogen ion, which must be looked for in the original substance or solution.

Properties and Reactions of the Metals and Ions of Group 6

MAGNESIUM

Metallic Magnesium.—Magnesium is a silver-white, malleable, ductile metal of specific gravity 1.74. It tarnishes in moist air and burns to magnesium oxid, MgO, with a brilliant white light rich in actinic rays. It dissolves in acids, but not in alkalis and is therefore wholly basic. It unites directly with chlorin and nitrogen. It is a powerful reducer, being able to separate boron and silicon from their oxids.

Magnesium Compounds.—Magnesium is bivalent and quite active, unites with many of the negative elements and forms salts with most of the acids. Its salts may be normal, acid, basic or double, and are generally soluble in water.

Magnesium Ion.—Magnesium forms one positive, simple, colorless ion, Mg^{++}. There are also possibly complex ions in the double salts.

Reactions of Magnesium Ion.—Use for the reactions 0.05 N solution of magnesium chlorid, $MgCl_2,6H_2O$, equivalent 101.6; or of magnesium sulfate, $MgSO_4,7H_2O$, equivalent 123.2.

*1. **Phosphate ion,** PO_4^{---}, precipitates white magnesium phosphate, $Mg_3(PO_4)_2$, easily soluble in acids, soluble in water 0.2 gram to the liter. If ordinary sodium phosphate, Na_2HPO_4, is used as the reagent, the precipitate will be largely hydrogen magnesium phosphate, $HMgPO_4$, which is rather soluble, about 3 grams to the liter of water. In the presence of am-

monium hydroxid crystallin ammonium magnesium phosphate, $NH_4MgPO_4,6H_2O$, forms, soluble in water 0.08 gram to the liter. In the presence of an excess of ammonium hydroxid this solubility is reduced to about 0.022 gram to the liter while in the presence of ammonium chlorid it is increased again to about 0.066 gram to the liter. This last is the average solubility of the ammonium magnesium phosphate in the solutions from which it is usually precipitated in the course of an ordinary analysis. The precipitate is soluble in acids, but is thrown down again when the acid is neutralized with ammonium hydroxid.

*2. **Ammonium hydroxid,** in the absence of ammonium salts, precipitates magnesium hydroxid, $Mg(HO)_2$, but incompletely because of the slight dissociation of the reagent. On addition of ammonium chlorid the precipitate dissolves, the excess of ammonium ions driving back the dissociation of the reagent until the quantity of magnesium hydroxid is below its solubility. Magnesium hydroxid dissolves easily in acids, but not in alkalis. It dissolves in water 0.009 gram to the liter.

3. **Alkali hydroxids** precipitate magnesium hydroxid as above, but more completely and not so soluble in ammonium chlorid.

4. **Barium hydroxid,** in the absence of ammonium salts, precipitates magnesium hydroxid completely.

*5. **Carbonate ions** precipitate from solutions sufficiently concentrated basic magnesium carbonates of varying composition, soluble in acids and in ammonium salts. Ammonium chlorid prevents the precipitation by formation of soluble ammonium carbonate and magnesium chlorid.

6. **Dry Reactions.**—Magnesium salts yield magnesium oxid in the blow-pipe flame. If this is moistened with cobalt nitrate and heated again in the outer flame, it assumes a pink color.

SODIUM

Metallic Sodium.—Sodium is a white metal with specific gravity 0.97, melting-point 95.6° and boiling-point 740°. It tarnishes quickly in the air and burns with a bright yellow flame to the oxids Na_2O and Na_2O_2. It decomposes water and acids with vigor and dissolves in liquid ammonia to a blue solution.

Sodium Compounds.—Sodium is chemically active and its compounds are very numerous. It unites with all the negative elements, forms alloys with many metals and yields salts of all the acids. Indeed, almost every compound of sodium which theory calls for has been actually prepared. The same is true of potassium.

Sodium Ion.—Sodium forms one positive ion, Na^{+}, univalent, colorless and very active. It is basic in all its chemical relations and it yields no anion either simple or complex. It displaces other metals generally from their compounds and is itself displaced with great difficulty.

Reactions of Sodium.—Since the salts of sodium are all soluble in water, almost any one of its compounds may be used for the reactions. Very convenient is a normal solution of sodium chlorid, NaCl, equivalent 58.45.

*1. **Potassium diantimonate,** $K_2H_2Sb_2O_7$, produces in concentrated neutral or slightly alkalin solutions of sodium salts a white crystallin precipitate of sodium diantimonate, $Na_2H_2Sb_2O_7,6H_2O$, soluble in water 2.5 grams to the liter. No other than alkali metals, no ammonium salts and no acid must be present, otherwise diantimonic acid or other diantimonates will be thrown down This is the only reagent which precipitates sodium and this reaction is not much used, since the flame reaction is generally conclusive and is more convenient.

2. **Sodium Flame.**—When heated in the Bunsen flame on platinum wire, sodium compounds give a characteristic brilliant yellow color. The test is very delicate and the student must guard against being misled by the traces of sodium which are almost always accidentally present. A crystal of potassium dichromate or a solution of the same appears yellow in sodium light.

3. **Sodium Spectrum.**—The sodium spectrum is a bright yellow line easily located and recognized. The only difficulty in identifying sodium by means of its spectrum lies in the fact that its line is always seen in the spectroscope. The student must judge

by contrast, observing whether the line is intensified when the substance is introduced.

POTASSIUM

Metallic Potassium. Potassium is a white metal with specific gravity 0.87, melting-point 62.5° and boiling-point 720°. Its vapor is green and it dissolves in liquid ammonia to a blue solution. Its properties are closely like those of sodium but it is chemically more active and more basic.

Potassium Compounds.—Potassium like sodium unites to all the negative elements, forms alloys with many metals, and replaces the hydrogen of water and acids. It decomposes water with such violence that the hydrogen is inflamed at once. Potassium and sodium hydroxids are the strong alkalis.

Potassium Ion.—Potassium forms one kation, K^+, univalent, colorless and very active. It is wholly basic and there are no complex ions.

Reactions of Potassium.—The potassium salts are all soluble in water. Use normal solution of any one, say potassium chlorid, KCl, equivalent 74.65.

*1. **Chlorplatinic acid,** H_2PtCl_6, gives in concentrated solutions a yellow, crystallin precipitate of potassium chlorplatinate, K_2PtCl_6, soluble in water about 10 grams to the liter, almost insoluble in alcohol or alcohol-ether. When heated the compound decomposes thus:

$$K_2PtCl_6 = 2KCl + Pt + 2Cl_2.$$

If the residue is treated with water and filtered from the platinum, the filtrate will again give the precipitate with chlorplatinic acid (difference from ammonium ion). Ammonium salts should not be present. To make the test add one or two drops of the reagent to a small quantity of the solution, evaporate nearly to dryness and add a little alcohol. If iodid ion is present, it will reduce the chlorplatinic to chlorplatinous ion the potassium salt of which is soluble in water and there will be no precipitate. The presence of the iodid ion will be recognized by the brown color which appears when the reagent is added. To remove it evaporate with a little concentrated nitric acid.

2. **Sodium hydrogen tartrate,** $NaHC_4H_4O_6$, gives in moderately concentrated solutions a white precipitate of potassium hydrogen tartrate, $KHC_4H_4O_6$, insoluble in alcohol, soluble in acids and in alkalis, and in water 11.1 grams to the liter. Ammonium salts should not be present. Carry out the tests as with chlorplatinic acid.

3. **Fluosilicic acid,** H_2SiF_6, precipitates, white gelatinous potassium fluosilicate, K_2SiF_6, difficultly soluble in water and in acids, insoluble in alcohol, soluble in water 1.25 grams to the liter. The solution must be acid, since hydroxid ion decomposes the reagent, setting free white gelatinous silicic acid.

*4. **Sodium cobaltinitrite,** $Na_3Co(NO_2)_6$, (fresh solution) precipitates yellow potassium cobaltinitrite, $K_3Co(NO_2)_6$, from concentrated potassium solutions containing acetic acid. The action is hastened by gentle heat. If an organic acid is present, the solution should be neutralized with sodium carbonate and then made acid with acetic acid before the reagent is added. If ammonium salts are present, they must be removed by evaporation and ignition.

*5. **Potassium Flame.**—When heated in the Bunsen flame on platinum wire potassium salts yield a characteristic violet color which is completely masked by the yellow if sodium is present. If the flame is viewed through a blue glass, or a solution of indigo or of gentian blue, the yellow rays are cut off, while the violet rays pass through, and potassium may thus be detected in the presence of sodium

6. **Spectrum of Potassium.**—The spectrum of potassium is a bright line in the red and two faint lines in the violet.

LITHIUM

Metallic Lithium.—Lithium is a soft white metal which melts at 180° and is not volatile at red heat. It is the lightest of solids, its specific gravity being only 0.534. It has properties similar to those of sodium but it is less active.

Lithium Compounds.—The compounds of lithium are exactly analogous to those of sodium. It salts are all soluble except the

carbonate and phosphate. The nitrate and chlorid are soluble in alcohol (difference from sodium and potassium).

Lithium Ion.—Lithium forms one positive colorless ion, Li^+, Lithium is basic in all its relations and forms no anion either simplex or complex.

Reactions of Lithium.—Use normal solution of lithium chlorid, LiCl, equivalent 42.5.

*1. **Carbonate ion** precipitates from concentrated solutions white lithium carbonate, Li_2CO_3, easily soluble in acids and in water about 13 grams to the liter.

2. **Phosphate ion** precipitates white lithium phosphate, Li_3PO_4, easily soluble in acids, and in water 0.4 gram to the liter. The presence of a little sodium hydroxid makes the reaction more delicate.

*3. **Lithium Flame.**—Lithium salts color the Bunsen flame carmin red, the color differing but little from that of the strontium flame.

*4. **Lithium Spectrum.**—Lithium is spectroscopically identified by a bright line in the red.

AMMONIUM

Ammonium Compounds.—The ammonium radical is closely related in chemical properties to sodium and potassium. Its compounds are all decomposed by heat, many of them undergoing a simple molecular dissociation, the parts uniting again when cooled,

(a) $NH_4Cl \rightleftharpoons NH_3 + HCl$ (b) $(NH_4)_2SO_4 \rightleftharpoons 2NH_3 + H_2O + SO_3$.

If the acid radical is an oxidizer, the ammonium radical is destroyed and the nitrogen or an oxid of nitrogen is set free, the reaction not being reversible,

$$NH_4NO_3 = 2H_2O + N_2.$$

If the acid radical is not volatile, the acid or oxid will remain.

Since ammonium salts may generally be removed from a mixture by moderate heating, they are useful for introducing certain anions into solutions of metallic ions.

Ammonium hydroxid cannot be obtained free from water

because it readily dissociates into ammonia and water and at 100° the dissociation is complete, all the ammonia being expelled from the solution. It is for this reason that ammonium hydroxid is called the **volatile alkali**.

Ammonia gas is recognized by its ammonia-like odor and its solubility in water to alkalin solution.

Ammonium Ion.—The ammonium ion, NH_4^+, has a valence 1 and is colorless and quite active. The hydroxid is a weak alkali because of its slight dissociation into ions. It forms complex ions through the displacement of its hydrogen by certain metals.

Reactions of Ammonium Ion.—Ammonium salts are all more or less soluble in water and it is only in concentrated solutions that any precipitates can be obtained. Ammonium chlorid may be used for the reactions as follows: For 1 a solution of any strength; for 2 a very dilute solution such as the distilled water of the laboratory; for 3 and 4 a concentrated solution; for 5 the dry solid.

*1. **Alkali hydroxids,** (KHO, NaHO, $Ca(HO)_2$, $Ba(HO)_2$, $Sr(HO)_2$), when heated with ammonium salts, dry or in solution, cause the evolution of ammonia gas. The presence of the ammonia is proved (1) by the characteristic stifling odor, (2) by its turning red litmus blue, (3) by its giving white fumes with hydrochloric acid.

*2. **Nessler's Test.**—Minute traces of ammonia are detected by means of Nessler's solution. Since certain metals interfere, it is best to distill off a few cubic centimeters from the solution, to which a little alkali hydroxid has been added, and test the distillate, which will contain most of the ammonia. Add a few drops of the reagent and observe the yellow color produced, looking downward through the tube toward a white surface. Absence of color means no ammonia and the depth of the color indicates the amount of ammonia present. By comparing the color with that produced in standard solutions of ammonia of known strength quantitative determinations are made.

If the solution is sufficiently concentrated, a dark red precipitate falls which has the composition HgO, $HgNH_2I$.

3. **Chlorplatinic acid,** H_2PtCl_6, precipitates from strong solutions yellow crystallin ammonium chlorplatinate, $(NH_4)_2PtCl_6$, soluble in water 6.66 grams to the liter. When the precipitate is strongly heated, it decomposes, leaving as residue only platinum (difference from potassium). Conduct the operation as with potassium.

4. **Hydrogen sodium tartrate,** $HNaC_4H_4O_6$, gives in concentrated solutions a white precipitate of ammonium hydrogen tartrate, $NH_4HC_4H_4O_6$, soluble in water, mineral acids and alkalis, insoluble in alcohol. The presence of sodium acetate aids the precipitation. This compound is distinguished from the corresponding potassium salt by leaving on ignition only a carbonaceous residue not alkalin when moistened

5. **Dry Reactions.**—All ammonium compounds are decomposed when heated on platinum. See page 153.

HYDROGEN

Free hydrogen may be recognized as follows:

1. It is a light gas, colorless, odorless, tasteless, very slightly soluble in water.

2. It burns with a pale blue flame and water is the sole product of its combustion.

Combined hydrogen generally separates as hydrogen ion or hydroxid ion and as such is identified. It also enters into certain compound ions and radicals, of which ammonium is the most familiar example.

Hydrogen Ion, H^+.—The presence of hydrogen ion is always indicated by what is known as the **acid reaction,** or the effect upon certain indicators, of which litmus is the one most commonly used. This ion colors litmus red and has a sour taste. It gives its electric charge to most metals and becomes molecular hydrogen. A rough estimate of the concentration of the hydrogen ion in a solution is made by observing the sourness of its taste and the intensity of its action on easily ionized metals such as zinc or iron. A solution which turns litmus red contains

hydrogen ion derived from an acid or an acid salt or a salt which hydrolizes in the acid direction.

Analysis of the Magnesium-Alkali Group

SEPARATION AND IDENTIFICATION ON THE METALS AND IONS OF GROUP 6

Elements: Magnesium, sodium, potassium, lithium, hydrogen.

Radical: Ammonium.

Ions: Mg^{++}, Na^{+}, K^{+}, Li^{+}, H^{+}, NH_4^{+}.

Group reagent: There is no group reagent and each ion must be identified by its special properties and reactions.

Principle.—Magnesium belongs to Group 5, but has been kept in solution by ammonium chlorid It is separated by precipitation. Sodium, potassium, lithium and ammonium form soluble salts, only a few of which can be precipitated, and then only in concentrated solution. Some are scarcely soluble in alcohol. Hydrogen ion is indicated by the acid reaction.

Preparation of the Solution.—The precipitation of Group 5 by ammonium carbonate is often incomplete, and before testing the filtrate for Group 6, it may be necessary to remove any barium and calcium which may remain in it. Concentrate a small portion by boiling and add a drop of dilute sulfuric acid. If there is a white precipitate indicating barium, treat the whole solution in the same manner and filter. To a portion of this filtrate, or of the other solution if barium is absent, add ammonium hydroxid to alkalin reaction and then ammonium oxalate. If a white precipitate of calcium oxalate appears, treat the whole solution, boil and filter.

The Analysis.—1. To a portion of the filtrate prepared as above add ammonium hydroxid, and if a precipitate of magnesium hydroxid falls add ammonium chlorid until it dissolves. Add sodium phosphate in excess and shake well. A white crystallin precipitate of ammonium magnesium phosphate, NH_4MgPO_4, indicates magnesium.

If lithium is present, lithium phosphate may fall and may be mistaken for magnesium. In this case evaporate to dryness, heat to drive off ammonium salts, cool, add two drops of dilute

hydrochloric acid and a few cubic centimeters of water and filter. Add to the filtrate equal quantities of solutions of ammonium carbonate, ammonium chlorid and sodium phosphate, shake well and let stand for a time. Ammonium magnesium phosphate will precipitate, while lithium will remain in solution.

2. Evaporate a portion of the prepared solution to dryness in platinum or porcelain, and heat until ammonium salts are expelled, or till fumes cease to come off. Care should be taken to heat the dish all over. If magnesium has been found it should be removed as follows: Dissolve the residue in a little hot water with a drop of hydrochloric acid, add barium hydroxid just to alkalin reaction, filter off the precipitated magnesium hydroxid, remove from the filtrate the excess of barium ion with a little ammonium carbonate or sulfuric acid and filter. Evaporate this filtrate to dryness and ignite to expel the ammonium or sulfate ions. If there is no residue, sodium, potassium and lithium are absent. If there is a residue, moisten a portion of it with hydrochloric acid and carry it into the flame on platinum wire. A bright yellow color indicates sodium; violet color, potassium; carmin red color, lithium.

3. If the flame of 2 is yellow, view it through the blue glass or potassioscope. A strong violet tinge indicates potassium. To confirm potassium dissolve a portion of residue of 2 in a little water, add a drop of acetic acid and a few drops of sodium cobaltinitrite. A yellow precipitate is potassium cobaltinitrite, $K_3Co(NO_2)_6$.

4. Lithium will be identified by its carmin red flame color, by the bright red line of its spectrum and by the solubility of its chlorid in alcohol.

5. As an alternative method for potassium moisten a little of the residue of 2 with water, add a drop of chlorplatinic acid, then a few drops of alcohol. A yellow precipitate of potassium chlorplatinate, K_2PtCl_6, indicates potassium.

6. Sodium, potassium and lithium are easily identified by means of the spectroscope. In most cases the original substance may be used.

7. Apply a portion of the original substance or solution to moistened blue litmus paper. A red color indicates hydrogen ion.

8. The ammonium ion has been introduced from time to time in the course of the analysis and cannot be looked for in the solution from which the other ions have been removed. To the original substance or solution in a test-tube add alkali hydroxid and heat to boiling. The evolution of ammonia gas, recognized by its pungent odor, by its turning red litmus blue and by its fuming with volatile acids, proves the presence of ammonium.

TABLE FOR GROUP 6

Ions: Mg^{++}, Na^{+}, K^{+}, Li^{+}, H^{+}, NH_4^{+}.

Remove traces of barium and calcium from the filtrate of Group 5 and divide in two portions.

Add to one portion NH_4OH and Na_2HPO_4. White, crystallin precipitate of NH_4MgPO indicates **magnesium.**	Evaporate the second portion to dryness, remove magnesium if necessary and ignite to expel ammonium salts. Test the residue in four portions. The original substance or solution may be used for the flame test.
Apply a little of the original substance or solution to moistened blue litmus paper. Red color indicates **hydrogen ion.**	*a.* Moisten a portion with HCl and apply flame test. Yellow indicates **sodium;** violet, **potassium.** View the flame through blue glass. Violet color indicates **potassium.**
To the original solution or substance add NaHO and boil. NH_3 which smells of ammonia, blues litmus and fumes with HCl indicates **ammonium.**	*b.* Dissolve a portion of the residue in water, add acetic acid and $Na_3Co(NO_2)_6$. Yellow $K_3Co(NO_2)_6$ indicates **potassium.**
	c. Moisten a portion of the residue with water, add H_2PtCl_6 and alcohol. Yellow K_2PtCl_6 indicates **potassium.** Filter, evaporate. Red Na_2PtCl_6 indicates **sodium.**
	d. Extract a portion of the residue with absolute alcohol, evaporate to dryness and test for lithium with flame or spectroscope. If lithium is present, it will be seen when examining for sodium and potassium.

PART III

ACIDIC ANALYSIS

Chapter XII

PROPERTIES AND REACTIONS OF THE NON-METALS, ACIDS AND ANIONS

We have seen that when an acid goes into solution in water it separates into two ions, one of which is hydrogen ion and the other a simple or compound anion. The latter are called **acid ions** and are identical with those of the corresponding salts. The more common anions may be classified as follows:

1. Negative elements, as Cl^-, Br^-, S^{--}.
2. Negative radicals acting as elements, as CN^-.
3. Oxyanions, as NO_3^-, SO_4^{--}, CNO^-.
4. Thioanions, as AsS_4^{---}, CNS^-, SnS_3^{--}.
5. Haloanions, as $PtCl_6^{--}$, BF_4^-.
6. Metallocyananions, as $Fe(CN)_6^{----}$, $Fe(CN)_6^{---}$, $Co(CN)_6^{----}$.

The grouping of these anions is given in the next chapter. They are taken up here in the order of the periodic system to simplify treatment and facilitate reference. In this connection also will be found the discussion of water, hydrogen peroxid and the negative elements with their oxids and sulfids.

OXYGEN

Free oxygen may be identified as follows:

1. It is a colorless, odorless, tasteless gas, sparingly soluble in water and of density a little above that of the air.
2. It supports and accelerates combustion.
3. It is rapidly absorbed by alkalin solution and pyrogallic acid.

Combined oxygen will generally be identified indirectly, since

it is a constituent of oxids, hydroxids and oxyanions. Its presence will be discovered without special tests.

Oxygen Ion, O^{--}.—Oxygen does not readily form the elemental ion. In its very dilute aqueous solution it is scarcely ionized at all. Its tendency is to unite with other elements to form compound ions.

Oxids.—Oxids are so various that no general rule can be given for their identification. If an element has been found which was not free in the original substance and not associated with another ion either positive or negative, the compound is most probably an oxid. If so it will exhibit the properties of the oxid of the element found.

Water, H_2O.—The following properties serve to identify water:

1. It is a neutral liquid without color, odor or taste.
2. It boils at 100° and freezes at 0°.
3. It gives to dehydrated copper sulfate a blue color.

Hydroxid Ion, HO^-.—The hydroxid ion is recognized by what is known as the **alkalin reaction.** It colors litmus blue, has an alkalin taste and is caustic toward organic matters. A rough estimate of the concentration may be made by observing the intensity of its soapy feel, and its caustic effect on the skin or tongue. A solution which turns litmus blue contains the ions of a base or of a salt which hydrolizes in the basic direction. A neutral solution, one which turns litmus neither red nor blue, contains neither an acid nor a base nor a salt which hydrolizes. (Except salts composed of weak ions which hydrolize without excess of hydrogen or hydroxid ion.)

Alkalinity may be due to hydrolysis and does not necessarily indicate the presence of a hydroxid. To detect a hydroxid in presence of a carbonate add excess of barium chlorid and a few drops of phenolphthalein solution. Red color indicates a hydroxid. The excess of barium chlorid prevents ionization of the precipitated barium carbonate.

Hydrogen peroxid, H_2O_2.—Hydrogen peroxid is commonly known only in dilute aqueous solution. It is quite unstable and is

both an oxidizing and a reducing agent. It oxidizes chromate to perchromate ion, reduces permanganate to manganous ion, turns potassium-iodid-starch solution blue and bleaches vegetable colors. The perchromate test is characteristic and is made as follows: To the liquid to be tested add a dilute acidulated solution of potassium dichromate and a few drops of ether and shake. The ethereal layer which separates on standing will be colored blue if hydrogen peroxid is present. If the solution is sufficiently concentrated, the blue color appears without the ether.

THE HALOGENS

Fluorin, chlorin, bromin and iodin constitute a natural group of elements and have many properties in common. They also present a fine illustration of the graduation of group properties. They form the binary or haloid acids and salts, all of which are called **halids.** They form ions readily and each one is changed from the ionic to the free state by any one of lower atomic weight:

(a) $Br^- + Cl = Br + Cl^-$, (b) $I^- + Cl = I + Cl^-$,
(c) $I^- + Br = I + Br^-$.

FLUORIN

Fluorin, F_2.—Fluorin is a yellowish green gas of great chemical activity, so active indeed that it is never met with free in the course of an analysis. It forms the fluorid ion, F^-, and a few fluoanions, such as BF_3^- and SiF_6^{--}.

Fluorids.—Fluorids are generally recognized by their action with sulfuric acid, being decomposed with liberation of hydrogen fluorid which etches glass. Other fluorin compounds undergo the same decomposition and this is a general test for fluorin in any form. The test is made as follows: Mix in an iron dish with a little concentrated sulfuric acid half a gram of calcium fluorid or of the dry substance supposed to contain fluorin, warm gently until fumes are seen (be careful not to breathe the fumes), then cover with a glass plate which has been previously coated with wax through which lines have been cut

with a sharp point. Leave for a few minutes, warming a few times until the fumes are just seen. On the removal of the wax, lines will be found etched in the glass:

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$

$$CaNa_2SiO_4 + 8HF = CaF_2 + 2NaF + SiF_4 + 4H_2O.$$

Fluorid Ion, F^-.—The fluorid ion is exceedingly active and very poisonous. The fluorids of hydrogen and of the alkali metals are readily soluble in water, those of the alkali earth metals insoluble and those of the heavy metals slightly soluble. The fluorid ion combines with silicon to form the complex fluosilicate ion, SiF_6^{--}, and in this way glass and porcelain are etched by hydrofluoric acid.

Use 0.1 N solution of ammonium fluorid, NH_4F, equivalent 37.

Barium chlorid precipitates barium fluorid, BaF_2, insoluble in alkalis, soluble in acids and in water 1.63 gram to the liter.

CHLORIN

Chlorin Gas.—Chlorin is a heavy, yellowish green gas of characteristic irritating odor, soluble in water 2.5 volumes to one at 10°. It is very active, attacks metals, destroys organic tissues, bleaches vegetable colors, sets iodin free, and turns potassium-iodid-starch blue. It is liberated when its compounds are decomposed in presence of an oxidizing agent. It unites with all the other elements except fluorin and the noble gases. The oxids and sulfids are unstable and may be identified by their properties given in the text-books.

Chlorids.—Chlorids, either dry or in concentrated solution, are identified by the following reactions:

1. The insoluble chlorids, except silver chlorid, are decomposed by boiling with sodium carbonate. Silver chlorid is reduced by fusion with sodium carbonate. By filtration the solution of the chlorid ion is obtained free from the metal and is identified as on page 163.

2. The chlorids of sodium, potassium and barium are but slightly soluble in hydrochloric acid. These may be separated from other chlorids by saturating the concentrated solution with HCl and filtering.

3. Chlorids, except those of silver, mercury, lead and tin, are decomposed by sulfuric acid with liberation of HCl.

4. Most chlorids when mixed with potassium dichromate and sulfuric acid yield, on warming, chromyl chlorid, CrO_2Cl_2, (difference from bromin and iodin).

Chlorid Ion, Cl^-.—The chlorids all dissolve in water, yielding the chlorid ion, except those of silver, lead, thallium, mercurous mercury, cuprous copper, and a few others which are hydrolytically decomposed, yielding an insoluble compound (Sb, Bi, Sn). The chlorids of phosphorus and arsenic are decomposed by water to form HCl and the acid of phosphorus or arsenic. The characteristic reagent for chlorid ion is silver ion, the two combining to form insoluble silver chlorid.

Use 0.1 N solution of sodium chlorid, NaCl, equivalent 58.45.

*1. **Silver nitrate** precipitates white silver chlorid, AgCl, properties of which have been given under silver. When silver chlorid is placed along with zinc in dilute sulfuric acid, it is decomposed by the nascent hydrogen.

*2. **Lead ion** precipitates from concentrated solutions lead chlorid, $PbCl_2$, for properties of which see lead.

*3. **Mercurous ion** precipitates white mercurous chlorid, Hg_2Cl_2, practically insoluble in water and in acids.

Hypochlorites.—Hypochlorites are all unstable and soluble in water and are decomposed by acids even carbonic with liberation of chlorin or hypochlorous acid. They are decomposed by heat into chlorid and chlorate and must be prepared and tested for in the cold.

Hypochlorite Ion, ClO^-.—Hypochlorous acid and all hypochlorites dissolve in water, yielding the unstable, active hypochlorous ion whose properties are mainly due to its instability and its oxidizing action. The commonest and most important hypochlorite is the so-called chlorid of lime or bleaching powder. It is a mixed compound, which is decomposed by water into calcium chlorid and calcium hypochlorite,

$$2Ca(ClO)Cl = CaCl_2 + Ca(ClO)_2.$$

Use 0.1 N solution of chlorid of lime, equivalent about 127.

1. **Dilute acids** liberate chlorin,

$$ClO^- + 2H^+ = Cl + H_2O.$$

2. **Potassium-iodid-starch** is turned blue because of oxidation of iodid ion to molecular iodin,

$$2I^- + ClO^- + H_2O = I_2 + Cl^- + 2HO^-.$$

3. **Vegetable colors** are strongly bleached by oxidation.

4. **Metallic hydroxids** are oxidized to higher forms,

$$2Fe(HO)_2 + NaClO + H_2O = NaCl + 2Fe(HO)_3.$$

5. **Silver nitrate** precipitates two-thirds of the chlorin as silver chlorid, leaving the other third in solution as silver chlorate,

$$3NaClO + 3AgNO_3 = 3NaNO_3 + 2AgCl + AgClO_3.$$

Chlorates.—The chlorates are characterized by instability and powerful oxidizing action. With combustibles they make detonating mixtures. They are decomposed by heat, yielding oxygen, and by acids, yielding chlorin or oxids of chlorin.

Chlorate Ion, ClO_3^-.—Chloric acid and all the chlorates dissolve in water with liberation of the colorless chlorate ion, which is unstable and a powerful oxidizer. Reducing agents convert it into chlorid ion.

Use the dry salt or a 0.1 N solution of potassium chlorate, $KClO_3$, equivalent 122.45.

*1. **Sulfuric acid** decomposes chlorates, setting free yellowish, unstable chlorin tetroxid, Cl_2O_4,

$$3KClO_3 + 2H_2SO_4 = KClO_4 + 2HKSO_4 + H_2O + Cl_2O_4.$$

2. **Hydrochloric acid** decomposes chlorates, liberating in variable quantities chlorin and chlorin tetroxid approximately in proportions represented by the following equation:

$$4KClO_3 + 12HCl = 4KCl + 6H_2O + 9Cl + 3ClO_2.$$

*3. Chlorates deflagrate on burning coals, make explosive mixtures with combustibles, and decompose when heated yielding oxygen.

4. Nascent hydrogen, sulfurous acid, ferrous salts, and the other reducing agents convert chlorate into chlorid ion.

Perchlorates.—Perchlorates are all more or less soluble in water and are more stable than the chlorates. The perchlorate ion, ClO_4^-, is rather stable but a powerful oxidizer.

Use the dry salt or a concentrated solution.

1. Perchlorates deflagrate on hot coals and at a high temperature lose oxygen and become chlorids.

2. **Sulfuric acid** acting on perchlorates liberates perchloric acid, $HClO_4$, a fuming, corrosive, volatile liquid.

3. **Hydrochloric acid** has no action, difference from chlorates, bromates and iodates.

4. **Potassium ion** precipitates from concentrated solutions the slightly soluble white, crystallin potassium perchlorate, $KClO_4$.

5. **Silver nitrate** produces no precipitate, difference from chlorids.

BROMIN

Bromin, Br.—Bromin is a heavy, reddish brown, opaque liquid with a penetrating, chlorin-like odor and a specific gravity 3.188. It is very volatile at the air temperature, passing to a dark vapor, and it boils at 59°. It dissolves in water, three parts to 100, imparting its color to the solution. It is chemically closely related to chlorin, but less active. It oxidizes and bleaches and gives a yellow color to starch. These properties suffice to identify free bromin.

Bromids.—Bromin unites with hydrogen, ammonium, cyanogen and the metals generally to form bromids. These in the solid state may be identified by the following reactions:

*1. **Sulfuric acid** decomposes bromids, setting free bromin and hydrogen bromid. The brown color of the bromin and its characteristic odor distinguish it from chlorin and iodin.

*2. **Sulfuric acid** and potassium dichromate decompose bromids with liberation of bromin (difference from chlorin).

Bromid Ion.—Hydrobromic acid and all the bromids, except those of silver, lead and mercurous mercury, dissolve in water with liberation of the colorless bromid ion, Br^-.

Use 0.1 N solution of potassium bromid, KBr, equivalent 119.

*1. **Silver nitrate** precipitates yellow silver bromid, AgBr, in-

soluble in dilute acids, soluble in ammonium hydroxid, in potassium cyanid, and in sodium thiosulfate.

*2. **Free chlorin** (chlorin water) added to a bromid solution sets bromin free, the chlorin assuming the ionic state:

$$Cl_2 + 2Br^- = 2Cl^- + Br_2.$$

If a few drops of carbon disulfid are added and shaken with the solution, they absorb the bromin and turn brown. Excess of chlorin must be avoided, lest bromin chlorid, BrCl, be formed, which will not color the disulfid.

Hypobromites.—Hypobromites have properties very similar to those of the hypochlorites. They are unstable, oxidize and bleach, and are decomposed by acids.

Hypobromite Ion.—Hypobromous acid (known only in solution) and all the hypobromites dissolve in water with separation of hypobromite ion, BrO^-. This ion is identified by reactions similar to those given under hypochlorite ion.

Bromates.—Bromates are somewhat more stable than chlorates. They are decomposed by heat with liberation of bromin or bromids or both. Acids decompose them giving in order bromic acid, hydrobromic acid, and finally bromin:

$$KBrO_3 + HCl = KCl + HBrO_3,$$
$$HBrO_3 = HBr + O_3$$
$$HBrO_3 + 5HBr = 3H_2O + 3Br_2.$$

Bromate Ions.—Bromic acid and bromates, except $AgBrO_3$ and $Hg_2(BrO_3)_2$, dissolve in water, liberating colorless bromate ion, BrO_3^-.

Use 0.1 N solution of sodium bromate, $NaBrO_3$, equivalent 151.

1. **Silver nitrate** precipitates white silver bromate, $AgBrO_3$, insoluble in dilute nitric acid, soluble in ammonium hydroxid and in potassium cyanid, decomposed by hydrochloric acid with liberation of bromin and chlorin (difference from silver halids) and by sulfuric acid with separation of bromin (difference from iodate).

2. **Sulfite ion, hydrogen sulfid** and **ferrous ion** reduce bromate ion to bromin or bromid ion.

3. **Manganese sulfate** gives with addition of a little sulfuric acid a red color and on boiling a brown precipitate of manganese dioxid. Iodates and chlorates give neither the color nor the precipitate. This test, which is very characteristic, was proposed by H. H. Willard, of the University of Michigan.

IODIN

Free Iodin.—Iodin is a dark gray crystallin solid with a peculiar odor resembling that of chlorin and bromin, specific gravity 4.95. It melts at 116° and boils at 180°, giving a heavy violet vapor. It is volatile at the air temperature and sublimes when heated. It dissolves in alcohol, in ether and in solution of potassium iodid, and in water one part in 5,500.

Free iodin may be identified by observing a sufficient number of the above properties. In solution or set free from solution it is readily identified by the following reactions:

1. **Sodium thiosulfate** decolorizes iodin solutions with formation of sodium tetrathionate and sodium iodid:

$$2Na_2S_2O_3 + 2I_2 = 4NaI + Na_2S_4O_6.$$

*2. **Starch paste** is colored an intense blue by free iodin.

3. **Carbon disulfid** in contact with free iodin receives a deep violet color.

Iodids.—The iodids are soluble in water except those of silver, gold, platinum and palladium. The iodids of bismuth and lead are sparingly soluble. The following reaction is characteristic:

*1. **Sulfuric acid** decomposes iodids with liberation of iodin and some hydrogen iodid.

Iodid Ion.—Hydrogen iodid and the soluble iodids dissociate in aqueous solution, yielding the colorless iodid ion, I^-. The presence of this ion is shown by a number of characteristic reactions.

Use 0.1 N solution of potassium iodid, KI, equivalent 166.

1. **Lead ion** precipitates yellow lead iodid, PbI_2, soluble in hot water, forming a solution from which on cooling golden yellow crystals separate.

*2. **Silver nitrate** precipitates yellow curdy silver iodid, AgI, insoluble in nitric acid, slightly soluble in ammonium hydroxid, soluble in potassium iodid, in potassium cyanid and in sodium thiosulfate. When shaken with chlorin water the iodin is displaced and may be detected with starch paste or carbon disulfid.

*3. **Mercuric chlorid** precipitates scarlet mercuric iodid, MgI_2, soluble in excess of the precipitant, or of potassium iodid, the complex ion HgI_4^{--} being formed. See under mercury.

4. **Copper sulfate** is reduced by iodids. See under copper. Since chlorin and bromin are not precipitated by the copper ion, this reaction may be used to detect iodin in their presence.

5. **Palladous ion** (palladium nitrate) precipitates black palladous iodid, PdI_2, somewhat soluble in excess of potassium iodid to form potassium iodopalladite, K_2PdI_4. Chlorids and bromids give no precipitate.

6. **Potassium nitrite** with sulfuric acid sets iodin free. To the liquid to be tested add a little starch paste, then a drop of the mixture of potassium nitrate and sulfuric acid; blue color indicates iodin.

7. **Potassium dichromate** with sulfuric acid liberates iodin.

8. **Chlorin water** sets iodin free, coloring starch paste blue. An excess of chlorin discharges the color because of formation of colorless iodin chlorid, ICl, or iodic acid, HIO_3. Bromin water also oxidizes iodid ion in iodin, but excess does not discharge the color.

Iodates.—Only the iodates of the alkali metals are soluble in water. Iodates are decomposed by heat, by reducing agents, and by acids, yielding generally an iodid or iodin or both.

Iodate Ion.—Iodic acid and alkali iodates dissolve in water, yielding the colorless iodate ion, IO_3^-. This ion is precipitated by ions of the metals generally except those of the alkali metals. It is easily reduced to iodid ion or free iodin.

Use 0.05 N solution of sodium iodate, $NaIO_3$, equivalent 207.

1. **Silver nitrate** precipitates white silver iodate, $AgIO_3$, sol-

uble in ammonium hydroxid, and in concentrated sulfuric acid, difficultly soluble in nitric acid.

2. **Barium chlorid** precipitates white barium iodate, $Ba(IO_3)_2$, slightly soluble in water and in nitric acid, insoluble in dilute alcohol, soluble in hydrochloric acid with evolution of chlorin. This reaction enables one to separate the iodate from the iodid ion since barium iodid is soluble.

3. **Hydrogen sodium sulfite** sets iodin free:

$$2NaIO_3 + 5HNaSO_3 = 3HNaSO_4 + 2Na_2SO_4 + H_2O + I_2.$$

Hydrogen sulfid acts in the same way.

Haloacids and Halosalts.—But few haloacids and halosalts are likely to be met with by the analyst. The more common ones are fluoboric, fluosilic and chlorplatinic acids and their salts. These will be described in their proper places.

MANGANESE

Manganese will have been found in the course of basic analysis and it only remains here to describe the methods of identifying its compound anions, of which the most important are the manganate and permanganate ions. See also under Manganese in Basic Analysis.

Manganate Ion.—Manganic acid has not been obtained free and the manganates are quite unstable. The manganate ion, MnO_4^{--}, does not remain long in solution unchanged. It oxidizes to permanganate ion, MnO_4^{-}, and in the presence of reducing agents changes to manganous ion, Mn^{++}. The manganate ion is green but in presence of an acid soon shows the familiar pink color of the permanganate ion.

Use a fresh solution of potassium manganate. Expose a portion to the air for a few minutes and add a drop of acid to another portion. The change from green to pink indicates the oxidation of manganate to permanganate ion.

Permanganate Ion.—Permanganic acid is quite unstable but the permanganates are permanent when kept away from reducing agents. Permanganate ion has a beautiful violet-pink color and is a powerful oxidizer. In its oxidizing action it is reduced usually to manganous ion, which is almost colorless. Permanganate

ion is identified by its familiar color and its loss of color in the presence of reducing agents.

Use 0.01 normal solution of potassium permanganate, $KMnO_4$, equivalent 31.6, made acid with sulfuric acid.

To separate portions of the solution acidified with H_2SO_4 add the following reagents and note the discharge of color:

a. Ferrous sulfate. *b*. Sulfurous acid. *c*. Oxalic acid.

If the solution is not acid, manganese dioxid is precipitated.

SULFUR

Free Sulfur.—Sulfur occurs in several allotropic forms for description of which the student is referred to the text-books on chemistry. Free sulfur as usually met with will exhibit the following properties: It has a yellow color, is insoluble in water and most acids, soluble in carbon disulfid. When heated in a test-tube it volatilizes, condensing in brown drops; when heated in an open tube or in the air it burns with a blue flame, giving the characteristic odor of sulfurous oxid. It is oxidized by nitric acid or bromin to sulfuric acid.

***Hepar Reaction.**—A general test for combined sulfur, known as the **hepar reaction**, may be made as follows: Fuse the substance with sodium carbonate on charcoal, transfer the fused mass to a silver coin and moisten with water. A black or brown stain on the silver indicates sulfur. The carbon reduces the sulfur compound, setting free sodium sulfid, which reacts with the silver to form black silver sulfid.

Sulfids.—The sulfids of the alkali metals are soluble in water, other sulfids are more or less soluble in acids concentrated or dilute. The sulfids of the alkali-earth metals are slowly acted on by water with formation of the hydroxid and hydrosulfid, both of which are somewhat soluble:

$$2CaS + 2H_2O = Ca(HO)_2 + Ca(HS)_2.$$

Sulfids generally are recognized by their action with (1) heat, (2) acids, (3) oxidizing agents.

1. With heat:

a. Most sulfids remain unchanged when heated away from air.

b. The sulfids of arsenic and mercury sublime.

c. Persulfids and polysulfids give sulfur which sublimes.

d. Sulfids of gold and platinum are decomposed, the sulfur subliming and the metal remaining.

e. All sulfids when heated in the air give sulfurous oxid.

2. Sulfids are generally decomposed by acids. The special reaction depends upon the acid and its concentration.

a. Dilute acids decompose all soluble and some insoluble sulfids with liberation of hydrogen sulfid, which is identified by its peculiar offensive odor and its precipitation of metallic sulfids from solutions of metallic salts.

b. Most sulfids are decomposed by concentrated acids. Sulfuric acid gives sulfurous oxid and sulfur:

$$Na_2S + 2H_2SO_4 = Na_2SO_4 + 2H_2O + SO_2 + S.$$

c. Most difficultly soluble sulfids are decomposed by hydrochloric acid and nascent hydrogen with evolution of hydrogen sulfid.

3. Oxidizing agents, such as nitric acid, the halogens, chromates, permanganates, ferric salts, decompose many sulfids, sulfur being first set free and then oxidized to sulfate ion.

Polysulfids.—The alkali and alkali-earth metals form polysulfids of composition more or less complex. They act like the sulfids generally with liberation of more sulfur. They are all soluble in water.

Hydrosulfids.—The hydrosulfids of the alkali and alkali-earth metals are all soluble in water. They are unstable and give reactions like the sulfids.

Sulfid and Hydrosulfid Ions.—Solutions of hydrogen sulfid contain the sulfid ion, S^{--}, and the hydrosulfid ion, HS^{-}, along with hydrogen ion. The dissociation is so slight, only about 0.07 per cent. in decinormal solution, that the hydrogen ions are scarcely able to give the acid reaction. The hydrosulfid ion combines only with the alkali and alkali-earth metals and it is at the same time quite unstable, so that it is the sulfid which is generally formed when hydrogen sulfid acts on salts of the metals. The sulfid ion is colorless and very active. It unites to the ions of the heavy metals to form undissociated sulfids. Al-

though the sulfid ion is low in concentration, it is supplied by further dissociation of hydrogen sulfid as fast as it is removed by union with the metallic ion and thus the precipitation is quite rapid, except in the case of certain metals, such as arsenic and antimony.

Use a saturated solution of hydrogen sulfid, which is about one-fourth normal, or pass the gas through the solution of the reagent.

1. **Dilute acids** decompose the soluble sulfids and hydrosulfids, setting free hydrogen sulfid.

*2. **Silver nitrate** precipitates black silver sulfid, insoluble in cold nitric acid and in ammonium hydroxid.

*3. **The kations,** except those of the alkali and alkali-earth metals and chromium and aluminum, precipitate metallic sulfids, some soluble and others insoluble in dilute acids. The solution should be alkalin, because an acid is formed in the reaction.

4. **Sodium nitroprussid,** $Na_2Fe(CN)_5NO,H_2O$, is colored blue by the sulfid ion but not by the hydrosulfid ion. Hydrogen sulfid solution contains mainly the HS ion and does not give this reaction, but the color appears when alkali hydroxid is added.

Sulfurous Oxid, SO_2.—Sulfurous oxid is given off in certain reactions involving compounds of sulfur. It is a colorless gas which is easily identified by its peculiar stifling odor, its reducing action, its solubility in water, and the reaction of its solution for sulfite ion. One volume of water dissolves about 45 volumes of the gas at 15°.

Sulfurous Acid, H_2SO_3.—Sulfurous acid is formed when sulfurous oxid is dissolved in water. The action is reversible and the gas is entirely expelled by heat, $SO_2 + H_2O \rightleftharpoons H_2SO_3$. Because of its instability the acid has the odor of sulfurous oxid and cannot be obtained free from water. The solution oxidizes slowly to sulfuric acid. Its reactions are those of the sulfite ion. The acid dissociates but slightly and the ion is mostly HSO_3^-.

Sulfites.—All sulfites are decomposed by dilute acids with evolution of sulfurous oxid, and this is the characteristic test for sulfites. Oxidizing agents convert them into sulfates. Heated

away from the air they decompose into sulfate and oxid, except alkali sulfites, which yield sulfate and sulfid,

$$(a)\ 3CaSO_3 = CaO + 2CaSO_4,$$
$$(b)\ 4Na_2SO_3 = 3Na_2SO_4 + Na_2S.$$

Sulfites, sulfurous acid and sulfurous oxid are all powerful reducing agents. On the contrary, they oxidize strong reducing agents. Sulfite solutions are generally alkalin by hydrolysis,

$$SO_3^{--} + H_2O = HSO_3^- + HO^-.$$

Sulfite Ion.—The sulfite ion, SO_3^{--}, is colorless, unstable and active. The alkali sulfites and most of the acid sulfites are soluble in water. The solutions contain also the hydrosulfite ion, HSO_3^-.

Use 0.05 N solution of sodium sulfite, Na_2SO_3, $7H_2O$, equivalent 126.

*1. **Acids** decompose the sulfite ion, liberating sulfurous oxid.

2. **Oxidizing agents** (halogens, nitric acid, permanganates,) convert sulfite into sulfate ion. See page 174.

*3. **Barium chlorid** precipitates from neutral or alkalin solutions barium sulfite, $BaSO_3$, soluble in dilute acids (difference from barium sulfate). The precipitate does not fall in solutions of sulfurous acid because an acid is formed in the reaction. If to the acid solution and oxidizing agent be added, and the mixture warmed, barium sulfate precipitates. This reaction serves for the identification of sulfites in presence of sulfates. Acidulate, add barium chlorid and filter off the barium sulfate. Add to the filtrate an oxidizing agent (chlorin or bromin water) and if a sulfite is present, more barium sulfate will precipitate.

4. **Strontium and calcium ions** give reactions similar to those of barium, but these sulfites are more soluble. Barium sulfite is practically insoluble in sulfurous acid, strontium sulfite is difficultly soluble, calcium sulfite dissolves easily. The order of solubility in water is the same, one liter at 18° dissolving 1.25 gram of $CaSO_3$, 0.033 gram of $SrSO_3$ and 0.022 gram of $BaSO_3$.

5. **Lead ion** precipitates white lead sulfite, $PbSO_3$, soluble in cold dilute nitric acid. On boiling the solution oxidation takes

place and lead sulfate separates. Lead sulfite is insoluble in sodium thiosulfate (difference from lead sulfate and lead thiosulfate).

6. **Silver nitrate** precipitates white crystallin silver **sulfite**, Ag_2SO_3, soluble in concentrated acids, in ammonium hydroxid and in excess of the sulfite. In the last two cases complex ions are formed. On boiling the solution sulfite is oxidized to sulfate ion and sulfurous oxid and silver separate:

$$2Ag_2SO_3 = Ag_2SO_4 + SO_2 + Ag_2.$$

*7. **Reducing Actions.**—The reducing action of sulfite ions is very characteristic. The following are examples:

a. Hydrogen sulfid decomposes sulfites with separation of sulfur.

b. Potassium permanganate solutions are decolorized, sulfate and dithionate ions being formed in varying proportions.

c. Potassium iodate is reduced to iodin and iodin to iodid ion. Prepare a test paper by dipping strips of paper in potassium iodate solution and then in starch paste. The moist paper is colored blue on contact with sulfurous oxid or acid or an acidified sulfite solution. By further action the iodin is converted into iodid ion and the color is discharged:

$$2IO_3^- + 5SO_3^{--} + 2H^+ = I_2 + 5SO_4^{--} + H_2O,$$
$$SO_3^{--} + I_2 + H_2O = SO_4^{--} + 2H^+ + 2I^-.$$

Summing these equations we have

$$2IO_3^- + 6SO_3^{--} = 6SO_4^{--} + 2I^-,$$

which represents the final result but does not show that the presence of hydrogen ion is necessary.

d. **Mercury** and **gold** solutions are reduced with separation of the metals and chromate ion is reduced to chromic ion.

8. **Oxidizing Action.—Nascent hydrogen** reduces sulfite ion to hydrogen sulfid. A bit of zinc and a little dilute hydrochloric acid are added to the solution and the evolved hydrogen sulfid is recognized by its peculiar odor and by its blackening lead acetate paper.

Sulfuric Acid.—Sulfuric acid, H_2SO_4, is a colorless, oily liquid of specific gravity 1.84. When heated it dissociates into SO_3 and H_2O, these parts reuniting on cooling. The distillate which comes over at the boiling-point contains 1.5 per cent. water. The commercial acid contains 4 to 6 per cent. of water. The acid absorbs moisture from the air, becoming dilute and lower in specific gravity. It chars organic substances and is a powerful chemical agent. It dissolves in water in all proportions, ionizing about half as highly as hydrochloric acid. It is dibasic and forms normal, acid and double salts.

Sulfuric acid is identified by the properties just given. The dilute acid is recognized by the charring produced when paper moistened with it is heated and by the reactions of the hydrogen and sulfate ions.

Disulfuric acid, $H_2S_2O_7$, has the same general properties as sulfuric acid. It is more active and when heated gives off fumes of sulfuric oxid, SO_3.

Sulfates.—Most sulfates are soluble in water, the exceptions being the sulfates of calcium, strontium, barium and lead, and the basic sulfates of mercury, bismuth and chromium.

Neutral sulfates of the alkali metals and the sulfates of the alkali earth metals are not decomposed by heat. Other sulfates generally undergo decomposition with liberation of sulfuric oxid, SO_3. When boiled with sodium carbonate solution sulfates are changed to sodium sulfate. All sulfates give the hepar reaction.

Sulfate Ion.—Sulfuric acid and soluble sulfates yield in solution the sulfate ion, SO_4^{--}, colorless and quite active. The hydrosulfate ion, HSO_4^-, occurs in solutions of the acid and of acid sulfates, but its reactions are similar to those of the sulfate ion and the student will not often be called upon to distinguish them.

Use 0.05 normal solution of sulfuric acid, H_2SO_4, two cubic centimeters in a liter of water; or of sodium sulfate, Na_2SO_4, $10H_2O$, equivalent 161.

*1. **Barium chlorid** precipitates white barium sulfate, $BaSO_4$, insoluble in water and dilute acids. If the solution is too strongly acid with HCl, barium chlorid may be precipitated, since the concentration of ions may exceed the solubility product for barium chlorid. On adding water it redissolves.

This is the characteristic reaction for sulfate ion. The fluosilicate ion, SiF_6^{--}, gives a similar precipitate, but barium fluosilicate is decomposed by heat, yielding silicon fluorid.

*2. **Lead acetate,** $Pb(C_2H_3O_2)_2$, precipitates white lead sulfate, $PbSO_4$, soluble in strong sulfuric acid, in hot hydrochloric acid, in caustic alkalis, in ammonium salts of organic acids, and in sodium thiosulfate (difference from lead sulfite). See under Lead.

Thiosulfates.—Free thiosulfuric acid, $H_2S_2O_3$, is unknown. When liberated it breaks down at once into water, sulfurous oxid and sulfur. The thiosulfates are more stable.

All thiosulfates except those of barium, lead and silver are quite soluble in water. The following reactions are characteristic:

1. All thiosulfates are converted by heat into sulfates and polysulfids.

*2. All thiosulfates are decomposed by acids with evolution of sulfurous oxid and separation of sulfur. Sulfites give off SO_2 without the sulfur.

Thiosulfate Ion.—Solutions of thiosulfates contain the thiosulfate ion, $S_2O_3^{--}$, colorless and unstable.

Use 0.1 N solution of sodium thiosulfate, $Na_2S_2O_3{,}5H_2O$, equivalent 124.

1. **Barium chlorid** precipitates white barium thiosulfate, BaS_2O_3, soluble in concentrated hydrochloric and nitric acids with separation of sulfur and sulfurous oxid,

$$BaS_2O_3 + 2HCl = BaCl_2 + H_2O + SO_2 + S.$$

With dilute acids thiosulfate is reduced to sulfite ion and sulfur separates slowly, $S_2O_3^{--} + H^+ = HSO_3^- + S$. Barium thiosulfate is rather soluble in water and the solution must not be too dilute.

2. **Silver nitrate** precipitates white silver thiosulfate, $Ag_2S_2O_3$, soluble in ammonium hydroxid, in nitric acid, and in excess of the reagent because of the formation of a complex ion which is probably $AgS_2O_3^-$. Both the precipitate and the complex ion are quite unstable. The former quickly turns black because of a reaction which yields silver sulfid and sulfuric acid,

$$Ag_2S_2O_3 + H_2O = Ag_2S + 2H^+ + SO_4^{--}.$$

The complex ion decomposes slowly, quickly when warmed, as follows:

$$2AgS_2O_3^- = Ag_2S + SO_4^{--} + SO_2 + S,$$

and the solution becomes clouded.

3. **Ferric ion** is reduced to ferrous ion, while the thiosulfate is converted into tetrathionate,

$$2S_2O_3^{--} + 2Fe^{+++} = S_4O_6^{--} + 2Fe^{++}.$$

When a ferric solution is added to a thiosulfate solution, a red color appears, which fades as the reduction takes place.

4. **Iodin** is reduced to iodid ion by a reaction similar to that of the ferric ion. A solution of iodin in potassium iodid is decolorized by thiosulfate, $2S_2O_3^{--} + 2I = S_4O_6^{--} + 2I^-$.

5. **Lead ion** (nitrate or acetate) precipitates white lead thiosulfate, PbS_2O_3, which is soluble in sodium thiosulfate and in nitric acid and which darkens because of a decomposition similar to that of the silver thiosulfate.

6. **Oxidizing agents** convert thiosulfate ion into sulfate ion.

SEPARATION OF THE IONS OF SULFUR

If the sulfid, sulfite, sulfate and thiosulfate ions occur together, they may be separated as follows:

1. Shake the solution with a little lead carbonate or add an ammoniacal solution of zinc chlorid. The sulfid precipitates and is separated by filtration.

2. Add to the filtrate of 1 barium chlorid. Sulfite and sulfate precipitate and are separated by filtration. If the solution is too concentrated, some barium thiosulfate may be found in the precipitate.

3. Treat the precipitate of 2 on the filter with hydrochloric acid. The sulfite dissolves and the sulfate remains.

4. To the filtrate from 3 add chlorin water. The sulfite ion is oxidized to sulfate ion and forms with the barium ion present insoluble barium sulfate.

5. To the filtrate from 2 add silver nitrate. White precipitate changing to black indicates thiosulfate ion.

A method of separating sulfite ion from sulfate and thiosulfate ions is proposed by Weston and Jeffreys in the Chemical News, Volume 97, page 85, 1908. The ions are precipitated with lead ion (nitrate or acetate) and the mixed precipitate is treated with 0.5 normal solution of sodium thiosulfate. The sulfate and thiosulfate of lead dissolves while the sulfite does not.

CHROMIUM

The element chromium and its kations have been treated in basic analysis and we speak here only of its most important anions.

Chromates and Dichromates.—Chromium trioxid, CrO_3, is a red crystallin solid soluble in water to an orange-red acid solution which probably contains chromic acid, H_2CrO_4, and possibly some dichromic acid, $H_2Cr_2O_7$. If the solution is neutralized with alkali hydroxid and evaporated, a yellowish crystallin alkali chromate separates. If the alkali chromate solution be acidified and evaporated, reddish yellow dichromate separates.

Heated with sulfuric acid in the presence of chlorids, chromates and dichromates yield dark red chromyl chlorid, CrO_2Cl_2, a liquid which boils at 117° and is decomposed by water into chromic and hydrochloric acids. Since bromids and iodids do not afford a similar reaction, this serves to identify chlorids in their presence.

Chromate and Dichromate Ions.—Hydrogen ion converts chromate into dichromate ion and hydroxid ion reverses the reaction,

$$2CrO_4^{--} + 2H^+ \rightleftharpoons Cr_2O_7^{--} + H_2O$$
$$Cr_2O_7^{--} + 2HO \rightleftharpoons 2CrO_4^{--} + H_2O.$$

This reaction serves to distinguish between chromate and di-

chromate ions, the color change being sufficiently marked and characteristic. See under Chromium in Basic Analysis.

In aqueous solution dichromates undergo hydrolysis with liberation of chromate ions and the reagent precipitates chromates rather than dichromates from such solutions.

Use 0.05 N solution of potassium chromate, K_2CrO_4, equivalent 97. For other properties of the precipitates see under each metal.

1. **Barium ion,** Ba^{++}, precipitates canary colored barium chromate, $BaCrO_4$, soluble in acids, except acetic, insoluble in alkalis.

*2. **Lead ion,** Pb^{++}, precipitates yellow lead chromate, $PbCrO_4$, soluble in strong acids and in alkalis, insoluble in ammonium hydroxid.

3. **Silver ion,** Ag^{+}, precipitates red silver chromate, Ag_2CrO_4, soluble in acids and in ammonium hydroxid.

4. **Mercurous ion,** Hg_2^{++}, precipitates a brown basic chromate which is changed by boiling to red mercurous chromate, Hg_2CrO_4, insoluble in alkalis, soluble in acids.

5. **Hydrogen peroxid,** H_2O_2, oxidizes chromate and dichromate ions to perchromate ions, which give the solution a blue color. See under hydrogen peroxid.

NITROGEN

Free Nitrogen is recognized by the following characteristics:

1. It is a colorless, odorless gas, only slightly soluble in water.
2. It is chemically inactive and a little lighter than the air.
3. It does not burn and does not support combustion.
4. Mixed with oxygen and subjected to electric sparks it forms oxids of nitrogen.

Oxids of Nitrogen.—Oxids of nitrogen are set free in decomposition of nitrites and nitrates. Those most common are N_2O_2, N_2O_3, and N_2O_4. They are recognized by their nitrous odor, and the brown fumes which they make in the air. It will not generally be necessary to distinguish the one from the other.

Nitrous Acid, HNO_2.—Nitrous acid cannot be obtained free and even in dilute solution soon decomposes, yielding nitric acid, nitrogen dioxid and water, $3HNO_2 = HNO_3 + N_2O_2 + H_2O$.

Nitrites.—Nitrites are all decomposed by acids, yielding nitric acid, nitrogen dioxid, water and a salt of the acid used. They are all oxidizing agents, parting with oxygen and becoming nitrogen dioxid. They are also reducing agents, taking oxygen and becoming nitrates.

All nitrates dissolve in water, those of silver and lead slightly.

Nitrite Ion.—Solutions of nitrous acids and of nitrites contain the nitrate ion, NO_2^-, colorless and unstable.

Use 0.1 N solution of sodium nitrite, $NaNO_2$, equivalent 69.

*1. **Acids,** particularly sulfuric, decompose nitrites in the cold, setting free first probably N_2O_3, which, in contact with the air, becomes N_2O_4, gases which are recognized by their brown color and nitrous odor.

2. **Silver Nitrate** precipitates crystallin silver nitrite, $AgNO_2$, soluble in water 0.2 grams to the liter.

3. **Indigo solution** is decolorized by oxidation.

*4. **Iodids** are oxidized with separation of iodin. If potassium iodid is added to a nitrite solution acidified with sulfuric acid the solution becomes brown and if starch paste be added a blue color appears. This reaction is produced by the other oxidizing agents and cannot be used for nitrite ion when it is known that any such are present.

5. **Ferrous ion** is oxidized to ferric ion as with nitric acid.

6. **Potassium permanganate** in warm acid solution is reduced,

$$2KMnO_4 + 5HNO_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5HNO_3 + 3H_2O.$$

*7. **Griess' Test for Nitrite Ions.**—A very delicate test for nitrite ion was proposed by Peter Griess. The reagent, sulfanilic acid mixture for preparation of which see Chapter XV.

The test is made as follows: To 50 cc. of the solution to be tested add 1 cc. of the reagent and mix well. In a few minutes the liquid will be colored red if nitrite ion is present.

8. **Metaphenylenediamin,** $C_6H_4(NH_2)_2$, produces in dilute acid nitrite solutions a yellow color, because of the formation of a diazocompound, the well known dye called "Bismarck Brown." For preparation of the reagent see Chapter XV.

Nitric Acid, HNO_3.—Nitric acid is recognized as follows:

1. It is a colorless liquid with stifling acid odor, often reddish in color because of decomposition.

2. It dissolves metals with vigor, converting them into nitrates, oxids or acids, and liberating brown oxids of nitrogen.

3. It is unstable and a powerful oxidizing agent.

Fuming nitric acid has a brown color, due to dissolved N_2O_4, and is more active than nitric acid.

Nitrates.—Nitrates are vigorous oxidizing agents, form explosive mixtures with combustibles, and deflagrate on burning coals. When ignited they yield oxygen and when heated with sulfuric acid the brown oxids of nitrogen are liberated. They are all soluble in water, but a few of them (bismuth and mercuric nitrates) are hydrolyzed with precipitation of difficultly soluble basic salts.

Nitrate Ion,—NO_3^-.—Nitric acid and nitrate solutions contain the nitrate ion, and since all nitrates are soluble, this ion cannot be identified by precipitation. It is generally recognized by its oxidizing action.

Use decinormal potassium nitrate, KNO_3, equivalent 101.

*1. **Ferrous ion** is oxidized to ferric ion with liberation of nitrogen dioxid, N_2O_2, which combines loosely with the excess of ferrous salt to an unstable brown substance. The operation may be conducted as follows: To the solution supposed to contain the nitrate ion add some ferrous sulfate solution, mix, and pour down the side of the test-tube two or three cubic centimeters of strong sulfuric acid so that it underlies the solution. If nitrate ion is present, a brown ring appears at the contact zone. The color disappears on application of heat. Nitrite ion gives the same reaction without the presence of sulfuric acid.

Bromids and iodids interfere with this reaction, since they are decomposed by the sulfuric acid with liberation of bromin and iodin, which color the solution. To remove these precipitate with silver acetate and remove the excess of silver with potassium chlorid.

Dichromate ion also interferes. This may be reduced to chromic ion with sulfurous oxid and the chromic ion removed with ammonium hydroxid.

*2. **Brucin** is a delicate reagent for nitrate ion. A 0.2 per cent. solution of brucin in pure sulfuric acid is used. A little of the solution to be tested is mixed with three times its volume of sulfuric acid and one cubic centimeter of the brucin solution added; or a few drops of the solution is added to two cubic centimeters of the brucin solution. The nitrate ion imparts to the solution a red color, which vanishes in a little while. Nitrite solutions to which sulfuric acid has been added always contain some nitrate ion and may give the brucin reaction. This must be remembered.

3. **Indigo,** C_8H_5NO, is decolorized by nitric acid and by nitrate solutions containing sulfuric acid, being converted into isatin, $C_8H_5NO_2$.

4. **Zinc dust** with sodium hydroxid reduces nitrate ion to ammonia: $4Zn + 7HO^- + NO_3^- = 4ZnO_2^{--} + 2H_2O + NH_3$. This reaction distinguishes nitrate ion from chlorate ion.

5. **Nascent hydrogen** (copper-zinc couple) reduces nitrate ion to nitrite ion. This test is very delicate and may be made as follows: A bit of zinc is added to a small quantity of the solution and then a drop of copper sulfate solution (the copper is precipitated on the surface of the zinc forming the copper-zinc couple) and the mixture gently boiled. A few drops of the solution added to potassium-iodid-starch solution colors it blue if nitrates are present. This test is only valid when nitrite ion is not present in the original solution.

Identification of Nitrite and Nitrate Ions When Both are Present.—The reaction for nitrite ion takes place readily in the presence of nitrate ion. To detect nitrate ion in the presence of nitrite ion is not so easy. All the operations used for removing the nitrite ion convert a portion of it into nitrate ion. Good results may be obtained as follows: Neutralize the solution, add ammonium chlorid, and heat to boiling until it does not give blue color at once when acidified and tested with K-I-starch

solution. Then test for nitrate ion. It is necessary to remember that some nitrate is formed and that the reaction must be very decided to indicate the presence of nitrates in the original solution. The reaction between nitrite and ammonium ions is as follows:

$$NO_2^- + NH_4^- = N_2 + 2H_2O.$$

PHOSPHORUS

Free Phosphorus is identified by the following characteristics:

1. It is a yellow, wax-like solid which fumes in the air with the odor of garlic.

2. It burns very readily, yielding a white powder soluble in water to an acid solution which reacts for anions of phosphorus. The red variety burns less easily, but yields the same product.

Phosphids.—Phosphids in passing into solution in water or acids are generally decomposed and the phosphid ion is scarcely known. In the decomposition hydrogen phosphid, H_3P, is often evolved, recognized by its garlic-like odor and its ready combustibility.

Oxids of Phosphorus.—Phosphorus forms two regular oxids, P_2O_3 and P_2O_5, both white, deliquescent, amorphous substances which dissolve in water to the corresponding phosphorous and phosphoric acids. These properties, together with those of the anions in the solution, are sufficient for the identification of these oxids.

Hypophosphorous Acid, H_3PO_2 or HPO, H_2O.—Hypophosphorous acid is monobasic, containing only one ionizable H. It is a powerful reducing agent, passing to phosphoric acid.

Hypophosphites.—Hypophosphites on ignition decompose, yielding phosphin and phosphate or diphosphate,

$$2NaH_2PO_2 = Na_2HPO_4 + H_3P.$$

Hypophosphite Ion.—All hypophosphites, including the acid, dissolve in water, yielding the hypophosphite ion, $H_2PO_2^-$, which is colorless and a reducing agent.

Use 0.1 N solution of sodium hypophosphite, NaH_2PO_2, equivalent 88.

1. **Sulfuric acid** oxidizes hypophosphite ion to phosphate ion, being itself reduced to sulfurous oxid,

$$2H_2SO_4 + H_2PO_2^- = H_2PO_4^- + 2SO_2 + 2H_2O.$$

2. **Salts of silver, copper, mercury and gold** are reduced, the metal being set free. With copper cuprous hydrid is first formed,

$$2H_2PO_2^- + 2CuSO_4 + 2H_2O =$$
$$2H_2PO_4^- + H_2SO_4 + SO_2 + Cu_2H_2.$$

This compound is distinguished from cuprous oxid by its darker color and by its yielding hydrogen when treated with hydrochloric acid.

3. **Caustic alkalis** at the boiling temperature oxidize hypophosphite to phosphate ion with evolution of hydrogen,

$$H_2PO_2^- + 2HO^- = PO_4^{---} + 2H_2.$$

4. **Nascent hydrogen** (zinc and dilute sulfuric acid) reduces hypophosphite ion to phosphin, $H_2PO_2^- + 5H = H_3P + 2H_2O$.

Phosphorous Acid, H_3PO_3.—Phosphorous acid is dibasic, only two of its hydrogen atoms being usually replaceable by metals. The acid and its salts are reducing agents, the phosphite becoming phosphate ion. On the other hand, it is reduced by nascent hydrogen to phosphin.

Phosphites.—Phosphites are crystallin salts which are easily oxidized and not easily reduced. They are all soluble in acids, but only the alkali phosphites are soluble in water. When ignited phosphorous acid and phosphites decompose, liberating phosphin,

$$4H_3PO_3 = 3H_3PO_4 + H_3P.$$
$$8Na_2HPO_3 = 4Na_3PO_4 + Na_4P_2O_7 + H_2O + 2H_3P.$$

Phosphite Ion.—Phosphorous acid and phosphites yield two anions, $H_2PO_3^-$ and HPO_3^{--}, the latter being the more abundant, and the one usually referred to as the phosphite ion.

Use 0.1 normal solution of sodium phosphite, Na_2HPO_3, $5H_2O$, equivalent 108.

1. **Barium chlorid** precipitates white barium phosphite, $BaHPO_3$, soluble in acids.

2. **Silver nitrite** precipitates at first white silver phosphite, $Na_2HPO_3 + 2AgNO_3 = 2NaNO_3 + Ag_2HPO_3$, which in con-

centrated cold solution and in hot dilute solution is reduced to metallic silver, $Ag_2HPO_3 + H_2O = H_3PO_4 + Ag_2$.

3. **Lead acetate** precipitates white lead phosphite, $PbHPO_3$, insoluble in acetic acid, soluble in the stronger acids.

4. **Sulfuric acid** is reduced by phosphorous acid and phosphites first to sulfurous acid and finally to hydrogen sulfid,

$$H_2SO_4 + H_3PO_3 = H_3PO_4 + H_2SO_3,$$
$$H_2SO_3 + 3H_3PO_3 = 3H_3PO_4 + H_2S.$$

5. **Strong alkalis** oxidize phosphite to phosphate ion, evolving hydrogen, $HO^- + HPO_3^{--} = PO_4^{---} + H_2$.

6. **Nascent hydrogen** (zinc and sulfuric acid) reduces phosphite ion to hydrogen phosphid, $HPO_3^{--} + 4H_2 = H_2P + 3H_2O$.

Phosphoric Acid, H_3PO_4.—Phosphoric acid is tribasic and forms normal, acid and double salts, one, two or all the hydrogen atoms being replaced. It is converted by heat into metaphosphoric and diphosphoric acids. In solution it ionizes by stages as follows:

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$$
$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{--}$$
$$HPO_4^{--} \rightleftharpoons H^+ + PO_4^{---}.$$

It is a weak acid and the dissociation, not very extensive at best, is mainly in the first stage. This is evidenced by the fact that it gives no precipitate with barium, lead and silver ions, the concentration of the ions HPO_4^{--} and PO_4^{---} not being high enough for the solubility products of the salts involved to be reached. The alkali phosphates readily yield precipitates with these metals, showing that they are ionized more highly in the second and third stages. Phosphoric acid is about 17 per cent. ionized in half normal solution.

Phosphates.—While phosphoric acid is tribasic the last hydrogen atom is not easily replaced and so the more common phosphates are monohydric. The term phosphate without the prefix usually implies the monohydric form. Thus common sodium phosphate is Na_2HPO_4. Heat converts the acid phosphates into

metaphosphates and diphosphates, but the normal phosphates are not so decomposed. All phosphates are soluble in acids but are reprecipitated when the acid is neutralized. Only the alkali phosphates are soluble in water.

Phosphate Ions.—Normal phosphates undergo hydrolysis in solution,

$$PO_4^{---} + H_2O \rightleftharpoons HPO_4^{--} + HO^-$$
$$HPO_4^{--} \quad H_2O \rightleftharpoons H_2PO_4^- + HO^-.$$

Phosphate solutions will therefore contain the ions PO_4^{---}, HPO_4^{--}, and $H_2PO_4^-$, and since they contain also the hydroxid ion they will be alkalin. As stated above, the more common ion is HPO_4^{--} and the salts precipitated will usually be monohydric.

For the reactions use a 0.05 normal solution of sodium phosphate, $Na_2HPO_4,12H_2O$, equivalent 119. The solution will be alkalin, because of hydrolysis.

1. **Silver nitrate** precipitates yellow normal silver phosphate, Ag_3PO_4, the hydrogen as well as the metal being replaced. The salt is soluble in nitric acid and in ammonium hydroxid, and the precipitate will be formed only in neutral solutions. Ammonium acetate aids the precipitation, driving the hydrogen into combination with the acetate ion.

2. **Lead acetate** precipitates white lead phosphate mostly normal, soluble in mineral acids, almost insoluble in acetic acid.

3. **Barium chlorid** precipitates white amorphous barium phosphate, $BaHPO_4$, easily soluble in acids, but thrown down again as normal phosphate, when the acid is neutralized with ammonium phosphate. If the solution is ammoniacal at first the normal phosphate is precipitated.

*4. **Magnesia mixture** precipitates white crystallin magnesium ammonium phosphate, $MgNH_4PO_46H_2O$, soluble in acids, but insoluble in weak ammonium hydroxid (2.5 per cent.). This reaction is sensitive and quantitative. See under Magnesium.

*5. **Ammonium molybdate,** $(NH_4)_2MoO_4$, in excess precipitates slowly from cold, rapidly from hot, nitric acid solutions

yellow crystallin ammonium phosphomolybdate, $(NH_4)_3PO_4$, $12MoO_3$, soluble in alkalis and in ammonium hydroxid. This is a characteristic reaction and is used for quantitative separations. Chlorids, bromids and iodids may interfere, being decomposed by the nitric acid. They may be removed by silver nitrate. Ferrocyanid ion also interferes. In this case use the barium precipitate, filtered, washed and dissolved in nitric acid.

*6. **Ferric chlorid** precipitates yellowish normal ferric phosphate, $FePO_4$, but not completely, since hydrochloric acid is formed in the reaction. See under ferric ion.

Diphosphoric Acid, $H_4P_2O_7$.—Diphosphoric acid is obtained by heating phosphoric acid to 213° until it has lost the requisite amount of water, $H_3PO_4 = H_4P_2O_7 + H_2O$. It is a white amorphous or crystallin solid which dissolves in water and in solution gradually changes to phosphoric acid. Although it is tetrabasic it forms but two series of salts, the hydrogen atoms being replaced in pairs.

Diphosphates.—Diphosphates are obtained by heating monohydrogen phosphates, $2Na_2HPO_4 = Na_4P_2O_7 + H_2O$. They are converted at a higher temperature into metaphosphates. Alkali diphosphates are soluble in water, the others in acids. Fused with sodium carbonate they are changed to phosphates.

Diphosphate Ions.—Since the hydrogen atoms of diphosphoric acid are replaced in pairs, there are only two ions, $H_2P_2O_7^{--}$ and $P_2O_7^{----}$. The precipitates are generally mixed, the normal diphosphate prevailing.

Use 0.05 N solution of sodium diphosphate, $Na_4P_2O_7$, $10H_2O$, equivalent 112.

*1. **Silver nitrate** precipitates silver diphosphate, $Ag_4P_2O_7$, soluble in ammonium hydroxid and in acids, slightly in acetic acid. The precipitate is white, thus differing from silver phosphate, which is yellow.

2. **Barium** and **lead ions** precipitate white salts soluble in acids.

3. **Ammonium molybdate** precipitates from hot solutions ammonium phosphomolybdate.

Metaphosphoric Acid, HPO_3.—Metaphosphoric acid is obtained by dissolving phosphoric oxid in cold water or by igniting phosphoric or diphosphoric acid at 400°. It is a white, amorphous, glassy solid commonly called glacial phosphoric acid. In solution it takes up water and becomes phosphoric acid.

Metaphosphates.—Metaphosphates are obtained by heating the dihydrogen phosphates or diphosphates,

$$(a)\ NaH_2PO_4 = NaPO_3 + H_2,$$
$$(b)\ Na_2H_2P_2O_7 = 2NaPO_3 + H_2O.$$

They are not easily decomposed by heat. Only the alkali and magnesium metaphosphates are soluble in water, all are soluble in acids.

Alkali metaphosphates fuse to a glassy mass which dissolves metallic oxids with characteristic colors. The so-called salt of phosphorous or microcosmic salt, sodium ammonium hydrogen phosphate, $NaNH_4HPO_4$, $4H_2O$, becomes sodium metaphosphate when heated in the Bunsen flame,

$$NaNH_4HPO_4,\ 4H_2O = NaPO_3 + 5H_2O + NH_3.$$

This fuses on platinum wire with metallic oxids to colored double phosphates. Copper oxid, for example, gives a blue bead containing sodium copper phosphate, $CuO + NaPO_3 = NaCuPO_4$. See Bead Reactions.

Metaphosphate Ion.—The metaphosphate ion, PO_3^-, is unstable in contact with water, gradually uniting with it and becoming phosphate ion. Fresh solutions must, therefore, be used for the reactions.

Use 0.05 N solution of sodium metaphosphate, $NaPO_3$, equivalent 102.

*1. **Silver nitrate** precipitates white silver metaphosphate, $AgPO_3$, soluble in ammonium hydroxid and in acids.

2. **Barium chlorid** precipitates white barium metaphosphate, $Ba(PO_3)_2$, soluble in acids and in excess of sodium metaphosphate.

3. **Magnesia mixture** produces no precipitate, distinction from phosphates.

4. **Ammonium molybdate** produces no precipitate in the cold, but in hot solutions ammonium phosphomolybdate falls.

*5. **Albumen** is coagulated by free metaphosphoric acid. This is a characteristic test and distinguishes this acid from phosphoric and diphosphoric acids. The coagulation is not produced by alkali metaphosphates except in presence of acetic acid.

ARSENIC

The characteristics of metallic arsenic and of its kations have been given in Basic Analysis. It remains here to consider its oxid and sulfid and its anions, the most important of which are arsenite, AsO_3^{---}, arsenate, AsO_4^{---}, thioarsenite, AsS_3^{---}, and thioarsenate, AsS_4^{---}.

Arsenous oxid, As_2O_3.—Arsenous oxid is identified by the following characteristics: (*a*) It is a white powder, (*b*) it volatilizes to a crystallin sublimate, (*c*) it is reduced by charcoal yielding a black sublimate, (*d*) it is slightly soluble in water to an acid solution which reacts for the arsenite ion.

Arsenous Sulfid, As_2S_3, and **Arsenic Sulfid,** As_2S_5, are yellow powders insoluble in dilute acids and soluble in ammonium sulfid. For further properties see arsenic in Basic Analysis.

Arsenous Acid, H_3AsO_3.—Arsenous oxid dissolves slightly in water making a weak solution of arsenous acid. The free acid cannot be obtained since it decomposes when the solution is evaporated. A stronger solution is obtained by dissolving arsenous oxid in potassium hydroxid and neutralizing the excess of alkali with nitric acid.

$$As_2O_3 + 3KHO = 2K_3AsO_3 + 3H_2O$$
$$K_3AsO_3 + 3HNO_3 = H_3AsO_3 + 3KNO_3.$$

The reactions of the acid are those of the arsenite ion. The acid is weak and but slightly ionized.

Arsenites.—Arsenites are insoluble in water except those of the alkali metals. They are easily oxidized to arsenates and are reduced by carbon to metallic arsenic. There are metarsenites and diarsenites, but it is not generally necessary to distinguish them in the course of an ordinary analysis. Arsenites like phos-

phites are usually not normal, but retain one or more of the hydrogen atoms of the acid.

Arsenite Ion, AsO_3^{---}.—Arsenite solutions contain the arsenite ion. Neutral solutions are but little ionized because of hydrolysis,

$$AsO_3^{---} + 3H_2O = H_3AsO_3 + 3HO^-.$$

If nitric acid is added to neutralize the hydroxid ion, the arsenite ion is almost completely changed into undissociated acid. If, on the contrary, hydroxid ion is added, the concentration of the arsenite ion is increased.

Use a 2 per cent. solution of commercial sodium arsenite, or prepare a solution as follows: Dissolve about 7 grams of arsenous oxid in a few cubic centimeters of alkali hydroxid, dilute with water, neutralize with nitric acid and make up to one liter.

1. **Hydrogen Sulfid.**—For reactions with this reagent see Basic Analysis.

2. **Silver nitrate** precipitates pale yellow silver arsenite, Ag_3AsO_3 soluble in acids, in ammonium hydroxid and in ammonium nitrate. With ammonium hydroxid a complex silver ammonium arsenite is formed probably $(AgNH_3)_3AsO_3$. The precipitation is aided by adding a few drops of dilute alkali hydroxid.

3. **Lead ion** precipitates white lead arsenite, $Pb_3(AsO_3)_2$, soluble in acids, even acetic.

4. **Solution of iodin** in potassium iodid is decolorized, the iodin being reduced to iodid ion.

5. **Copper sulfate** precipitates green copper hydrogen arsenite, $CuHAsO_3$ (Scheele's green), soluble in acids, in alkali hydroxids and in ammonium hydroxid. If the mixture is boiled the arsenite is oxidized to arsenate and the copper is reduced to cuprous oxid, Cu_2O, which precipitates.

Arsenic Acid, H_3AsO_4.—Arsenic acid is tribasic, but like phosphoric acid tends to retain one or two atoms of hydrogen in its salts. The insoluble salts are generally, however, precipitated normal. When ignited the acid gives off water becoming first

diarsenic acid, $H_4As_2O_7$, and then metarsenic acid, $HAsO_3$. In solutions these pass back to the tribasic acid.

Arsenates.—There are normal, acid and double arsenates isomorphous with the phosphates. There are also diarsenates and metarsenates. All these act in very much the same way with reagents. Only the alkali arsenates are soluble in water.

Arsenate Ions.—Arsenate solutions contain the arsenate ion, AsO_4^{---}, along with more or less of the ions $HAsO_4^{--}$ and $H_2AsO_4^{-}$.

Use 0.05 normal solution of disodium arsenate, Na_2HAsO_4, $12H_2O$, equivalent 134. An arsenate solution may be made as follows: Dissolve 7 grams arsenous oxid in alkali hydroxid, add nitric acid in excess, boil, dilute, nearly neutralize with alkali hydroxid, then make up to one liter.

1. **Hydrogen sulfid** reactions have been given in Basic Analysis.

2. **Silver nitrate** produces in neutral or very slightly alkalin solutions a brown precipitate of silver arsenate, Ag_3AsO_4, soluble in acids, with difficulty in acetic acid.

3. **Lead ion** precipitates white lead arsenate, $Pb_3(AsO_4)_2$, soluble in acids, with difficulty in acetic acid.

4. **Copper sulfate** precipitates copper hydrogen arsenate, $CuHAsO_4$ soluble in ammonium hydroxid without precipitation of cuprous oxid because arsenate ion is not a reducing agent.

*5. **Magnesia mixture** or magnesium ion in presence of ammonium chlorid and ammonium hydroxid gives a white crystallin precipitate of magnesium ammonium arsenate, amalogous to the corresponding phosphate, insoluble in ammonium hydroxid. When strongly heated this compound is changed to magnesium diarsenate, $Mg_2As_2O_7$. This reaction is practically complete and is used in the quantitative determination of arsenic. The arsenite ion gives no precipitate with magnesium ion, a fact which serves to distinguish between arsenites and arsenates.

*6. **Ammonium molybdate** precipitates from hot nitric acid solutions yellow, crystallin ammonium arseno-molybdate, $(NH_4)_3(MoO_3)_{12}AsO_4$, soluble in ammonium and alkali hy-

droxids, from which solution it is precipitated with magnesia mixture as above.

Arsenate Ion in Presence of Arsenite Ion.—To identify arsenate ion in presence of arsenite ion add hydrochloric acid and then potassium iodid. A yellow color due to free iodin indicates arsenates. The reaction is as follows:

$$AsO_4^{---} + 2H^+ + 2I^- = AsO_3^{---} + I_2 + H_2O.$$

ANTIMONY

The characteristics of antimony and of its kations have been given in Basic Analysis. Its principal anions are antimonite, SbO_3^{---}, antimonate, SbO_4^{---}, thioantimonite, SbS_3^{---}, and thioantimonate, SbS_3^{---}.

Oxids and sulfids of antimony are similar to the oxids and sulfids of arsenic and may be identified in like manner.

Antimonous Acid, H_3SbO_3.—When ammonium hydroxid, or alkali hydroxid or carbonate is added to a solution of antimonous chlorid, a white precipitate is obtained of $Sb(HO)_3$ or H_3SbO_3. This compound is soluble in both acids and alkalis a fact which indicates that antimony is both basic and acidic. the reactions may be represented as follows:

With acids—$Sb(HO)_3 + 3H^+ = Sb^{+++} + 3H_2O$.

With bases—$H_3SbO_3 + 3HO^- = SbO_3^{---} + 3H_2O$.

The antimonite ion of the second reaction is unstable and is hydrolytically decomposed and precipitated thus:

$$2SbO_3^{---} + 3H_2O = Sb_2O_3 + 6HO^-.$$

The antimonite ion will, therefore, rarely be found in a solution and no reactions for it will here be given.

Antimonic Acid, H_3SbO_4.—The acids of pentavalent antimony correspond to those of phosphorous. They are antimonic acid, H_3SbO_4, diantimonic acid, $H_4Sb_2O_7$, metantimonic acid, $HSbO_3$. The last two are obtained successively by heating the first. They are all white solids insoluble in water and weakly acidic. They cannot be made by union of the oxid with water since antimonic oxid is insoluble. Antimonates are decomposed by acids with separation of antimonic acid.

Antimonates.—Antimonates, diantimonates and metantimonates are all unstable and are more or less hydrolyzed by water. They are easily decomposed by acids with formation of antimonic acid. All except the alkali salts are insoluble in water.

Antimonate Ions.—Because of the slight solubility of all compounds of pentavalent antimony the ions are very illy defined and the reactions are more molecular than ionic. Theoretically, however, we may suppose solutions to contain the ions SbO_4^{---}, $HSbO_4^{--}$, $H_2SbO_4^{-}$, or SbO_3^{-}. The reactions are generally the same as those of the antimonic ion for which see Basic Analysis.

Distinction Between Antimonite and Antimonate Ions.—Antimony will have been found, if present, in the course of basic analysis. It is only necessary here to show how to ascertain in what form it is present.

1. If an ammoniacal solution of silver nitrate is added to an antimony solution, the antimonite ion is oxidized to antimonate ion and metallic silver separates, $SbO_3^{---} + 2Ag^{+} + H_2O = SbO_4^{---} + 2H^{+} + 2Ag$. Antimonate ion precipitates silver antimonate which redissolves in the ammonium hydroxid.

2. Acidify the solution to be tested and add potassium iodid. If antimonate ion is present, the iodin is set free and the solution is colored brownish red, the antimonate being reduced to antimonite ion, $SbO_4^{---} + 2H^{+} + 2I^{-} = SbO_3^{---} + H_2O + 2I$.

Thioacids and Thiosalts.—The thioacids and thiosalts of arsenic, antimony and tin are formed in the process of analysis of the second group metals. They will not often be found in original substances submitted for analysis. They are soluble in alkalis and are decomposed by acids usually with separation of sulfur.

CARBON

Free Carbon.—Carbon exists in three allotropic forms, (*a*) diamond, (*b*) graphite, (*c*) amorphous carbon in a variety of conditions such as charcoal, lampblack, mineral coal and so forth. At air temperature it is chemically very inactive, being scarcely

attacked by acids, alkalis or the halogens. At high temperatures it is quite active with some of the elements such as oxygen, sulfur and several of the metals. When porous or finely divided, it burns rather easily in the air to carbon dioxid.

Free carbon may be identified by the following characteristics:

1. It is a dark gray or black solid (except the diamond which is often in transparent crystals) of low specific gravity, insoluble in water, acids and alkalis.
2. It burns to carbon dioxid.
3. It reduces metallic oxids when heated with them.

Carbon Monoxid, CO.—Carbon monoxid is a decomposition product of many organic substances and is also produced by reduction of carbon dioxid with red hot carbon. It is a colorless, poisonous, gas with a slightly pungent odor. It is practically insoluble in water and burns with a pale blue flame to carbon dioxid. There is no corresponding acid.

Carbon Dioxid, CO_2.—Carbon dioxid is always a product of the combustion of carbon and of compounds of carbon. It is most conveniently prepared by treating carbonates with acids. It is a colorless, heavy gas, incombustible and not a supporter of combustion. It dissolves volume to volume in water at the ordinary temperature making a slightly acid solution. From solutions of the metals, except the alkali metals, it precipitates carbonates. The usual test reagent for it is lime-water from which it precipitates white calcium carbonate, $CaCO_3$.

Carbon Disulfid, CS_2.—Carbon disulfid is formed by direct union of carbon and sulfur at a high temperature. It is a colorless (generally slightly yellow), highly refractive liquid with a somewhat unpleasant odor. It is quite volatile and highly combustible. It burns with a blue flame to carbon dioxid and sulfurous oxid, the former being recognized by making a precipitate in lime-water and the latter by its stifling, sulfurous odor.

Carbids.—Carbon unites at high temperatures with many of the metals. The carbids are all insoluble in water and the carbid ion probably does not exist. The so-called calcium carbid, CaC_2,

undergoes decomposition in contact with water, but it is rather calcium acetylid and not a carbid proper.

Carbonic Acid, H_2CO_3.—Carbonic acid is obtained by dissolving carbon dioxid in water. Under pressure a moderately strong solution may be had, but when the pressure is removed the oxid escapes until the solution contains only its own volume of the gas. It is familiar to us as **carbonated water.** It is recognized by its sour, sharp taste and by the precipitate of calcium carbonate which it yields with lime-water.

Carbonates.—Carbonic acid is dibasic and forms normal, acid and double salts. The alkali and alkali-earth carbonates are usually acid salts especially when they are obtained from solution. Only the alkali carbonates are soluble in water, but some insoluble carbonates dissolve in water containing carbon dioxid, the more soluble hydrocarbonate being formed. Carbonates are generally soluble in acids with effervescence and escape of carbon dioxid. A few dissolve with difficulty, but when pulverized and heated they easily yield to the action of the acid. Some metals such as lead, copper and zinc form basic carbonates. All carbonates except those of the alkali metals are decomposed by heat into the metallic oxid and carbon dioxid. The action is reversible, the parts recombining when the mixture cools,

$$CaCO_3 \rightleftharpoons CaO + CO_2.$$

The usual tests for carbonates are (*a*) effervescence with acids and (*b*) decomposition by heat, CO_2 being evolved in both cases.

Carbonate Ions.—The carbonate ions are HCO_3^- and CO_3^{--}. They probably both occur in all aqueous carbonate solutions. The former is quite unstable so that precipitates are generally normal carbonates, except with those metals which form basic carbonates.

Use 0.1 N solution of sodium carbonate, Na_2CO_3, equivalent 53.

*1. **Acids** decompose the carbonate ion liberating carbon dioxid.

$$CO_3^{--} + 2H^+ \rightleftharpoons H_2O + CO_2.$$

2. **Metallic ions,** other than those of the alkali metals, precipi-

tate carbonates insoluble in water, soluble in acids with effervescence and escape of carbon dioxid.

SILICON

Silicon.—The analyst will seldom be called upon to identify silicon. Should a sample be presented, it will be recognized by its properties as given in any text-book of chemistry. Silicon is tetravalent in all its compounds and wholly acidic.

Silicids.—Silicon unites to hydrogen and to many of the metals to form silicids. Hydrogen silicid is a colorless gas which takes fire spontaneously in the air. Metallic silicids are solids generally insoluble in water. The silicids of the alkali-earth metals are decomposed by dilute hydrochloric acid with evolution of hydrogen silicid.

Silicon Fluorid, SiF_4.—Silicon fluorid is formed by the action of hydrofluoric acid on silicic oxid or silicates. It is a colorless gas which is immediately decomposed on contact with water, with formation of silicic and fluosilicic acids,

$$3SiF_4 + 4H_2O = 2H_2SiF_6 + H_4SiO_4.$$

Fluosilicic Acid, H_2SiF_6.—Fluosilicic acid is formed as just stated by the action of water on silicon fluorid. It is known only in solution since it decomposes on evaporation. The reactions of the fluosilicate ion serve for the identification of fluosilicic acid.

Fluosilicates.—The fluosilicates are generally soluble in water, those of potassium, sodium, ammonium, lithium, barium and calcium dissolving with more or less difficulty. The strontium salt is soluble so that this acid may be used to separate barium from strontium.

Fluosilicates are decomposed by hot sulfuric acid with formation of hydrogen fluorid, silicon fluorid and sulfates,

$$H_2SO_4 + Na_2SiF_6 = 2HF + SiF_4 + Na_2SO_4.$$

Fluosilicate Ion, SiF_6^{--}.—Fluosilicic acid and fluosilicates are rather highly dissociated in solution and contain the fluosilicate ion, SiF_6^{--}, colorless and quite active.

Use 0.1 N solution of sodium fluosilicate, Na_2SiF_6, equivalent 94.7.

*1. **Sulfuric acid** decomposes all fluosilicates, dry or in solution, with evolution of hydrogen fluorid and silicon fluorid, the former of which is recognized by its property of etching glass. See equation under fluosilicates, page 196.

*2. **Barium chlorid** precipitates crystallin barium fluosilicate, $BaSiF_6$, insoluble in water (1 part in 3,800) almost insoluble in dilute hydrochloric acid, soluble in strong hydrochloric acid (distinction from barium sulfate).

3. **Potassium chlorid** precipitates potassium fluosilicate, K_2SiF_6, difficultly soluble in water (1 part in 800) insoluble in alcohol and in excess of potassium chlorid, soluble in ammonium chlorid.

4. **Ammonium hydroxid** decomposes the fluosilicate ion with separation of gelatinous silicic acid,

$$Na_2SiF_6 + 4NH_4HO = 2NaF + 4NH_4F + H_2O + H_2SiO_3.$$

5. **Alkali hydroxids** do not precipitate silicic acid because of the formation of soluble alkali silicates,

$$4NaHO + Na_2SiF_6 = Na_4SiO_4 + 2NaF + 4HF.$$

Silicic oxid, SiO_2.—Silicic oxid occurs in nature in a great variety of forms the more important of which may be classified as follows: (*a*) crystallin; quartz and tridymite; (*b*) massive or cryptocrystallin; chalcedony, agate, jasper, flint, etc.; (*c*) amorphous; opal, infusorial earth, silicious sinter, etc.

Silicic oxid possesses the following characteristics:

1. As quartz it occurs massive or in hexagonal prisms surmounted by hexagonal pyramids.

2. In most of its forms it has a glassy fracture and is hard enough to scratch glass.

3. It is insoluble in water and in acids and is only slightly soluble in alkalis. Hydrous varieties dissolve in strong acids.

4. Hydrofluoric acid converts it into fluosilicic acid, H_2SiF_6.

5. It fuses with alkali carbonates to a soluble glass.

Artificially prepared silicic oxid is a white powder which possesses the above characteristics except as to physical condition.

Silicic Acids.—There are several silicic acids of which the most important are orthosilicic acid, H_4SiO_4, and metasilicic acid, H_2SiO_3. They are insoluble in water but form colloidal solutions from which they are precipitated in gelatinous form by heat, by acids, and by ammonium salts. They are decomposed by heat into water and silicic oxid. Since silicic oxid is insoluble in water, the acids cannot be obtained directly. They are formed by the action of acids upon silicates and fluosilicates. They are weakly acidic and but slightly ionized.

Silicates.—Silicates are very numerous and are often of complex composition. All except the alkali silicates are insoluble in water and many are insoluble in acids, more soluble in alkalis. They are decomposed by hydrofluoric acid with evolution of silicon fluorid, and when fused with alkalis or alkali carbonates they form alkali silicates which are soluble in water. Hydrous silicates dissolve in hydrochloric acid with separation of gelatinous silicic acid.

Removal of Silicates.—Silicates may be divided into two classes, (*a*) those decomposed by acids, including silicic acids, alkali silicates and hydrous silicates; (*b*) those not decomposed by acids, including anhydrous silicates generally. For the identification of silicates there are three methods, the first applicable to those soluble in acids, the other two to all silicates.

1. Digest the solution or the finely divided powder with strong hydrochloric acid. Filter, evaporate to dryness and heat gently for a time to insure that all the silicon is separated as silicic oxid. Treat with strong hydrochloric acid again, add water and filter. The precipitate is silicic oxid. The filtrate contains the chlorids of the metals present and is free from silicon.

2. The finely powdered substance is stirred with several times its weight of an equimolecular mixture of sodium and potassium carbonates and heated in a platinum crucible until effervescence ceases and the mass comes to quiet fusion. The crucible is dipped in cold water while still hot to make the fused mass separate from its wall, then crucible and contents are placed in a beaker and water and hydrochloric acid added. The mass dis-

solves with separation of gelatinous silicic acid which is treated as under 1 on preceding page. The filtrate contains the metallic ions which were present together with sodium and potassium ions and is free from silicon.

3. The second method cannot be used if alkalis are present and are to be identified. In this case the substance is treated with hydrofluoric acid, which decomposes the silicate with formation of volatile silicon fluorid. The reaction may be represented as follows:

$$CaSiO_3 + 6HF = CaF_2 + 3H_2O + SiF_4.$$

If sulfuric acid be also added, the metallic fluorid is decomposed and the remainder of the fluorin goes off as hydrogen fluorid,

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF.$$

The powdered silicate in a dish or crucible of platinum, iron or lead, is moistened with a mixture of equal volumes of sulfuric acid and water, then 5 to 10 cc. of hydrofluoric acid are added in small portions, while the mixture is heated on the water-bath and stirred with platinum wire, until the fluorids are no longer evolved. The crucible or dish is then heated over the free flame or on the asbestos board until the excess of sulfuric acid is expelled. The evaporation must be conducted under the hood and care must be taken not to inhale the fumes which are very poisonous. The residue of sulfates free from silicon is dissolved in water. If a portion remains undissolved it is tested for barium sulfate and titanic acid.

Silicate Ions.—The more common silicate ions are SiO_4^{----} and SiO_3^{--}. They occur in solutions of alkali silicates and are quite unstable, tending to units to hydrogen ion to form undissociated and very difficultly soluble silicic acid.

Use a freshly diluted solution of water glass, Na_2SiO_3.

1. On standing for a while white gelatinous silicic acid separates being formed by hydrolysis:

$$SiO_3^{--} + 2H_2O \rightleftharpoons H_2SiO_3 + 2HO^-.$$

2. On adding an acid to a portion of the solution drop by drop just to neutralization the precipitate is presently formed:

$$SiO_3^{--} + 2HNO_3 \rightleftharpoons H_2SiO_3 + 2NO_3^-.$$

3. Add ammonium salt. The precipitate is formed by hydrolysis according to 1, the ammonium ion uniting to hydroxid ion to form undissociated ammonium hydroxid and thus aiding hydrolysis.

4. Barium ion and lead ion precipitate barium and lead silicates both decomposed by acids with separation of silicic acid.

5. Silver nitrate precipitates yellowish silver silicate soluble in acids from which solution the silicic acid presently separates.

Stannites, stannates, plumbites and plumbates are unimportant compounds which have been sufficiently treated under tin and lead. They are unstable and are decomposed by acids with liberation of the corresponding kations.

BORON

Boron, B.—Boron is trivalent and wholly acidic. If the element is submitted for examination, it will be identified by its properties as given in any text-book of chemistry.

Boric Oxid, B_2O_3.—Boric oxid is obtained by burning boron or by igniting boric acid as a white powder or a glassy solid. It dissolves in water to form boric acid and may be identified as such.

Boric Acid, H_3BO_3.—Boric acid is a soft, white, crystallin powder slightly soluble in water, 4 parts in 100 at 15°, 33 parts in 100 at 100°. It is more soluble in alcohol and the solution burns with a green flame. It is a very weak acid being only 0.013 per cent. ionized in decinormal solution.

When boric acid is heated it loses water and becomes at first metaboric acid, HBO_2, then tetraboric acid, $H_2B_4O_7$, or some other meta form, and finally boric oxid, B_2O_3. These all dissolve in water to reform orthoboric acid.

Borates.—All borates are metasalts, the more important ones being the tetraborates, of which borax, $Na_2B_4O_7,10H_2O$, is the best known. Only the alkali borates are soluble in water, but because of the weakness of boric acid, all the salts are decomposed by acids with separation of boric acid,

$$Na_2B_4O_7 + 2HCl + 5H_2O = 2NaCl + 4H_3BO_3.$$

Alkali borates fuse with intumescence to a colorless, glass-like metaborate which has the property of dissolving metallic oxids with characteristic colors. See bead reactions.

Solid borates including boric acid may be identified as follows:

Moisten with strong sulfuric acid; the borate is decomposed and boric acid is set free. Add alcohol, stir and warm; volatile ethyl borate and water are formed,

$$H_3BO_3 + 3C_2H_5HO \rightleftharpoons (C_2H_5)_3BO_3 + 3H_2O.$$

The sulfuric acid absorbs the water and prevents the reversal of the reaction. The escaping mixture of alcohol and ethyl borate burns with a flame tinged with green.

The development of the green color of the borate flame requires a high temperature and the test will be more successful if conducted as follows: Place the material in a test-tube and fit a stopper through which passes a glass tube drawn to a point with small opening. Lower over the jet a tube a little larger so that the escaping vapors will draw air in after the manner of the Bunsen burner. The flame is applied at the top of the outer tube. If chlorid ion is present ethyl chlorid, C_2H_5Cl, may be formed and this also colors the flame green. Confirm as follows: Mix the powdered borate with an equal quantity of calcium fluorid and three times its weight of acid potassium sulfate, moisten with water and transfer a portion on a loop of platinum wire to Bunsen flame. Boron fluorid is formed and gives the green color. The reaction may be expressed as follows:

$$6CaF_2 + 14KHSO_4 + Na_2B_4O_7 = 4BF_3 + 6CaSO_4 + 7K_2SO_4 + Na_2SO_4 + 7H_2O.$$

Borate Ion.—When alkali borates dissolve in water, they undergo a complex hydrolysis and the solution is alkalin. A solution of borax, for example, seems to contain boric acid, sodium metaborate and sodium hydroxid. The hydrolysis may be represented by two equations thus:

$$Na_2B_4O_7 + 3H_2O \rightleftharpoons 2NaBO_2 + 2H_3BO_3$$
$$NaBO_2 + H_2O \rightleftharpoons NaHO + H_3BO_3.$$

The greater the dilution the greater the dissociation, so that very dilute solutions seem to contain only boric acid and sodium hydroxid.

Boric acid may ionize in three stages yielding with the hydrogen ion the ions $H_2BO_3^-$, HBO_3^{--} and BO_3^{---}. Precipitates are almost always metaborates and we may suppose that the prevailing ion in the solutions is the metaborate ion, BO_2^-, formed by hydrolysis as above.

Use 0.5 normal solution of borax, $Na_2B_4O_7$, $10H_2O$, equivalent 191. Dissolve the weighed borax in a quantity of water a little less than that required, neutralize with nitric acid and then dilute to the proper volume. The solution should be slightly alkalin or there will be no precipitate as borates are soluble in acids.

1. **Barium chlorid** precipitates white barium metaborate, $Ba(BO_2)_2$, insoluble in alkalis, slightly soluble in water, easily soluble in acids even acetic. Calcium ion acts in a similar way. If the precipitate does not appear at once, add a little ammonium hydroxid.

2. **Lead ion** precipitates white lead metaborate, $Pb(BO_2)_2$, soluble in acids, even acetic, soluble in strong alkalis, insoluble in ammonium hydroxid.

3. **Silver nitrate** precipitates white silver metaborate, $AgBO_2$, easily soluble in acids, and in ammonium hydroxid, decomposed by alkalis with separation of silver oxid.

4. **Turmeric paper** is colored reddish brown when dipped in a solution of boric acid or of a borate acidified with hydrochloric acid and dried at the temperature of boiling water. The color is not discharged by dilute acids (difference from alkalis). Alkali hydroxids deepen the color to a bluish black. Zirconic, titanic, tantalic, columbic and molybdic acids give the same reaction, but they are seldom present.

CYANOGEN AND ITS COMPOUNDS

Cyanogen, C_2N_2.—Cyanogen, CN^-, is a negative radical which resembles the halogens in its properties and reactions and in its

compounds. It unites with hydrogen to hydrocyanic acid and to the metals to form cyanids.

Free cyanogen has the formula, C_2N_2, two radicals combining to form the molecule. It is a colorless gas with almond-like odor. It burns with a peach-blossom colored flame. It is obtained by decomposing some of its compounds by heat.

Hydrocyanic Acid, HCN.—Hydrogen cyanid is a colorless, very volatile liquid which boils at 27°, smells like bitter almonds and is violently poisonous. It dissolves readily in water making the solution called hydrocyanic acid. It is a very weak acid being ionized only 0.01 per cent. in decinormal solution. It is unstable, soon passing by hydrolysis into ammonia and formic acid,

$$HCN + 2H_2O = HCOOH + NH_3.$$

It is prepared by heating cyanogen compounds with acids.

Cyanids.—Hydrocyanic acid has many properties in common with the haloid acids and exchanges its hydrogen for metals to form cyanids. Cyanids of the noble metals such as silver, gold, platinum and mercury are decomposed by heat yielding the metal and cyanogen,

$$Hg(CN)_2 = Hg + C_2N_2.$$

Other cyanids fuse without decomposition but when heated in the air are oxidized to cyanate,

$$KCN + O = KCNO.$$

They are, therefore, strong reducing agents and are used in blow-pipe reactions. Cyanids of the baser metals are decomposed when heated away from the air into the carbid of the metal and nitrogen, or into the metal, carbon and nitrogen.

(*a*) $Fe(CN)_2 = FeC_2 + N_2$. (*b*) $Pb(CN)_2 = Pb + C_2 + N_2$.

Cyanids are decomposed by hydrogen sodium carbonate, $HNaCO_3$, with evolution of hydrogen cyanid (difference from ferrocyanids, ferricyanids and thiocyanates).

Alkali and alkali earth cyanids dissolve in water with hydrolysis yielding the metallic hydroxid and hydrocyanic acid,

$$KCN + H_2O = KHO + HCN.$$

Cyanid Ion.—Hydrocyanic acid and soluble cyanids yield the

cyanid ion, CN^-. This ion resembles the ions of the halogens, but differs from them in having a tendency to form complex ions with various metals. See below. The insoluble cyanids may be brought into solution by hot dilute acids. Strong sulfuric acid breaks up the compound separating the carbon and nitrogen.

Use 0.1 N solution of potassium cyanid, KCN, freshly prepared, equivalent 65. This solution will be alkalin because of hydrolysis as explained above.

*1. **Silver nitrate** precipitates white silver cyanid, AgCN, insoluble in dilute nitric acid, soluble in ammonium hydroxid, and in potassium cyanid. The silver cyanid is reprecipitated when the solution is neutralized with nitric acid. See under Silver Ions.

2. **Prussian Blue Reaction.**—The cyanid is converted into ferrocyanid by action of a ferrous salt,

$$FeSO_4 + 6KCN = K_2SO_4 + K_4Fe(CN)_6.$$

From this solution a ferric salt precipitates Prussian blue or ferric ferrocyanid,

$$3K_4Fe(CN)_6 + 4FeCl_3 = Fe_4(FeC_6N_6)_3 + 12KCl.$$

The test may be carried out as follows: To the alkalin solution add a little ferrous sulfate and boil, then add hydrochloric acid and ferric chlorid. A blue precipitate indicates the presence of the cyanid ion.

3. **Thiocyanate Reaction.**—Thiocyanates give with ferric salts a deep red color due to the formation of ferric thiocyanate,

$$3KCNS + FeCl_3 = 3KCl + Fe(CNS)_3.$$

The thiocyanate is formed by the action of yellow ammonium sulfid on the cyanid,

$$(NH_4)_2S_2 + KCN = (NH_4)_2S + KCNS.$$

To the cyanid add a little ammonium sulfid and evaporate to dryness on the water-bath. Add hydrochloric acid and a drop of ferric chlorid solution. The test is delicate and the red color appears if even a trace of cyanid is present.

Cyanic Acid, HCNO.—Cyanic acid is an unstable, colorless liquid with penetrating odor recalling that of acetic acid. It is decomposed by water with liberation of carbon dioxid.

$$HCNO + 2H_2O = NH_4HO + CO_2.$$

Cyanates.—Oxidizing agents convert cyanids into cyanates which are rather stable compounds not being decomposed by a moderate heat. They all dissolve in mineral acids with effervescence and escape of carbon dioxid, the ammonia formed at the same time uniting with the acid anion,

$$KCNO + 2HCl + H_2O = NH_4Cl + CO_2 + KCl.$$

Some cyanic acid is also evolved and may be recognized by its odor. If the escaping gas is passed through silver nitrate solution, silver cyanid precipitates and thus cyanates are distinguished from carbonates.

Cyanate Ion, CNO^-.—Cyanate ion is unstable in presence of hydrogen ion, decomposing as indicated under cyanates.

Use O.1 N solution of potassium cyanate, KCNO, equivalent 81.

1. **Silver Ion,** Ag^+, precipitates white, curdy silver cyanate, AgCNO, soluble in ammonium hydroxid and in dilute nitric acid, the last distinguishing cyanate from cyanid ion.

2. **Cobalt Acetate,** $Co(C_2H_3O_2)_2$, colors cyanate solutions blue because of formation of cobaltocyanate, $K_4CoC_4N_4O_4$. If the solution is diluted, the color vanishes, but is restored on addition of alcohol or of more of the cyanate. Thiocyanates act in the same way, but not cyanids, nor cyanates in the presence of cyanids.

Thiocyanic Acid, HCNS.—Thiocyanic acid is a colorless, unstable, volatile liquid which dissolves in water in all proportions and is more stable in solution. It is a strong acid ionizing about to the same extent as hydrochloric acid.

Thiocyanates.—The thiocyanates are soluble in water except those of silver, lead, mercury, copper and gold. They are decomposed by heat and by strong acids. The alkali salts fuse unchanged in a closed vessel, but in contact with the air are converted into sulfate and cyanate. The thiocyanates of mercury

burn when heated and swell up in a wonderful manner (Pharoah's serpent).

Thiocyanate Ion, CNS^-.—Thiocyanate solutions contain the ion CNS^-, colorless, active and poisonous.

Use 0.1 N solution of potassium thiocyanate, KCNS, equivalent 97.

1. **Silver nitrate** precipitates white, curdy silver thiocyanate, AgCNS, insoluble in dilute nitric acid, soluble in ammonium hydroxid, and in water 0.00014 gram to the liter.

*2. **Ferric ion** colors the solution a deep red because of the formation of ferric thiocyanate, $Fe(CNS)_3$. This reaction is characteristic and delicate and is much used for the detection of ferric ion.

3. **Mercuric ion** precipitates white mercuric thiocyanate, $Hg(CNS)_2$, which dissolves in potassium thiocyanate forming the complex salt, $KHg(CNS)_3$.

Complex Cyanids.—Metallic cyanids dissolve in alkali cyanids, forming complex compounds the more important of which fall under the following acid types:

1. $HR'(CN)_2$ 2. $H_2R''(CN)_4$ 3. $H_3R'''(CN)_6$
4. $H_4R''(CN)_6$.

Of these the first two are very unstable and decompose as soon as set free.

$$1.\ HR(CN)_2 = HCN + RCN,$$
$$2.\ H_2R(CN)_4 = 2HCN + R(CN)_2.$$

Hence all the cyanids of these types will evolve hydrogen cyanid when decomposed by acids. Acids of the third and fourth types are more stable and are obtained free by acidifying the solution with mineral acids. On warming, however, decomposition takes place and hydrogen cyanid is evolved.

The salts of these acids with metals such as silver, gold, nickel, zinc and cadmium are obtained by dissolving the oxids in potassium cyanid,

$$NiO + 4KCN + H_2O = 2KHO + K_2Ni(CN)_4.$$

Salts of the other metals are obtained by dissolving the cyanid or some other salt in potassium cyanid.

Solutions of the salts contain the complex metallo-cyanid ions which react for neither the metal nor cyanogen until they are decomposed by acids.

Ferrocyanic Acid, $H_4Fe(CN)_6$.—Warm dilute acids decompose ferrocyanids with separation of ferrocyanic acid,

$$K_4Fe(CN)_6 + 4HCl = H_4Fe(CN)_6 + 4KCl.$$

The acid is unstable and not an article of commerce.

Ferrocyanids.—Only the alkali ferrocyanids are soluble in water. With metallic salts these undergo decomposition with

$$K_4Fe(CN)_6 + 2CuCl_2 = 4KCl + Cu_2Fe(CN)_6.$$

Insoluble ferrocyanids are converted into soluble ferrocyanids by treatment with alkali hydroxids or carbonates,

$$Fe_4(FeC_6N_6)_3 + 12NaHO = 4Fe(HO)_3 + 3Na_4Fe(CN)_6.$$

The metallic hydroxid is removed by filtration and the solution contains the ferrocyanid ion which is identified as below. Uranyl ferrocyanid gives potassium uranate instead of the hydroxid and zinc ferrocyanid yields potassium zincate along with the alkali ferrocyanid. The uranate is insoluble and may be removed by filtration, while the zinc may be precipitated with carbon dioxid and removed as zinc carbonate.

Ferrocyanids give the following reactions:

1. They are decomposed when heated with sulfuric acid,

$$K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O = 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO.$$

The escaping CO burns with blue flame.

2. When ignited in a tube they yield iron carbid, a cyanid and nitrogen,

$$K_4Fe(CN)_6 = 4KCN + FeC_2 + N_2.$$

The metallic cyanid may itself be thermolized,

$$2AgCN = Ag_2 + C_2N_2.$$

Ferrocyanid Ion, $Fe(CN)_6^{----}$.—Solutions of ferrocyanic acid and of ferrocyanids contain the complex ion, $Fe(CN)_6^{----}$, which has special reactions of its own and does not react for iron. This ion is of a light yellow color and responds to all the reactions mentioned under ferrocyanids.

Use for the tests 0.1 N solution of potassium ferrocyanid, $K_4Fe(CN)_6$, $3H_2O$, equivalent 105.5.

1. **Silver ion** precipitates white silver ferrocyanid, $Ag_4Fe(CN)_6$, sparingly soluble in nitric acid and in ammonium hydroxid (difference from silver cyanid), soluble in potassium cyanid. Nitric acid oxidizes it to silver ferricyanid which is soluble in ammonium hydroxid.

2. **Lead ion** precipitates white lead ferrocyanid, $Pb_2Fe(CN)_6$, insoluble in dilute, soluble in strong, nitric acid, practically insoluble in ammonium hydroxid.

3. **Cupric ion** precipitates brown cupric ferrocyanid, $Cu_2Fe(CN)_6$, insoluble in acids, soluble in ammonium hydroxid.

4. **Uranyl ion,** UO_2^{++}, precipitates brown uranyl ferrocyanid, $(UO_2)_2Fe(CN)_6$, which is changed by potassium hydroxid into yellow potassium diuranate, $K_2U_2O_7$.

5. **Ferrous ion** precipitates white ferric ferrocyanid, $Fe_2Fe(CN)_6$ which turns blue at once in the air because of oxidation to ferric ferrocyanid.

*6. **Ferric ion** precipitates blue ferric ferrocyanid, $Fe_4(FeC_6N_6)_3$, (Prussian blue). See under ferric reactions. This is the characteristic test for ferrocyanid ion.

7. **Oxidizing agents** convert ferrocyanid into ferricyanid ion.

Ferricyanic Acid, $H_3Fe(CN)_6$.—Ferricyanic acid is formed when hydrochloric acid acts upon potassium ferricyanid as an unstable, crystallin, solid soluble in water. Its reactions are the same as those of the ferricyanids and the ferricyanid ion.

Ferricyanids.—Ferricyanids are formed by oxidation of ferrocyanids.

$$K_4Fe(CN)_6 + Cl = KCl + K_3Fe(CN)_6.$$

The ferricyanids of the alkalis, of the alkali-earths and of ferric iron are soluble in water; all the others are insoluble.

The action of the ferricyanids with acids and alkalis is exactly analogous to that of the ferrocyanids. The insoluble ferricyanids are rendered soluble by treatment with alkali hydroxids.

Ferricyanid Ion, $Fe(CN)_6^{---}$.—Solutions of ferricyanic acid

and of ferricyanids contain the reddish yellow complex ion, $Fe(CN)_6^{---}$, which does not react for iron.

Use 0.1 N solution of potassium ferricyanid, $K_3Fe(CN)_6$, equivalent 109.6. The solution should be freshly prepared.

1. **Silver ion** precipitates orange-yellow silver ferricyanid, $Ag_3Fe(CN)_6$, insoluble in nitric acid, soluble in ammonium hydroxid (difference from silver ferrocyanid) and in potassium cyanid.

2. **Cupric ion** precipitates green cupric ferricyanid, $Cu_3(FeC_6N_6)_2$, insoluble in dilute acids and in ammonium salts, soluble in ammonium hydroxid.

*3. **Ferrous ion** precipitates from acid and neutral solutions blue ferrous ferricyanid, $Fe_3(FeC_6N_6)_2$. See under Ferrous Reactions.

4. **Ferric ion** produces no precipitate because ferric ferricyanid is soluble in water (difference from ferrocyanid ion).

5. In **alkali solutions** ferricyanids are easily reduced to ferrocyanids by reducing agents. For this reason it is often difficult to identify insoluble ferricyanids, since in bringing them into solution with alkali hydroxids they are reduced.

ORGANIC ACIDS

Organic acids contain the univalent carboxyl radical, COOH′, the H of which separates in solution as hydrogen ion, while the remainder of the molecule constitutes the anion of the acid. The following will illustrate the ionization:

Acetic acid, $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$.

Sodium acetate, $CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$.

Organic acids are generally weak, the dissociation and the concentration of hydrogen ion being small. The more common acids and those which will be treated here are formic, acetic, oxalic, tartaric and citric.

All organic acids and their salts are decomposed by heat, generally with carbonization.

FORMIC ACID

Formic Acid, HCOOH.—Formic acid is a colorless liquid with

a peculiar pungent odor and sharp sour taste. It is monobasic and forms numerous formates. Its reactions are those of its ions. In decinormal solution it is about 4.6 per cent. ionized.

Formates.—Formates are all soluble in water, but those of lead and silver are low enough in solubility to be precipitated in strong solutions. They exhibit the following characteristic reactions:

1. Formates are powerful reducing agents, giving up hydrogen and becoming carbon dioxid,

$$2HgCl_2 + 2HCOOH = Hg_2Cl_2 + 4HCl + 2CO_2.$$

2. Formates are decomposed by sulfuric acid, even in the cold, with evolution of carbon monoxid recognized by the blue flame with which it burns.

Formate Ion, $HCOO^-$.—Solutions of formic acid and of formates contain the formate ion, $HCOO^-$, whose reactions are not very characteristic.

Use 0.5 N solution of potassium formate, HCOOK, equivalent 84.

1. **Lead ions** precipitate from rather strong solutions white lead formate, $Pb(HCOO)_2$, soluble in acids and in 36 parts of water.

2. **Silver ion** precipitates white silver formate, $AgCHO_2$, which rapidly blackens on exposure to light, decomposing as follows:

$$2AgOOCH = Ag_2 + HOOCH + CO_2.$$

3. **Mercuric chlorid** is reduced to mercurous chlorid when boiled with a solution containing formate ion and the latter precipitates. See 1 under Formates above.

4. **Ferric ion** gives a brown solution of ferric formate, $Fe(CHOO)_3$, from which basic salt precipitates on boiling as in the case of the acetate ion.

ACETIC ACID

Acetic Acid, CH_3COOH.—Acetic acid is a colorless liquid with the odor and taste of vinegar. It boils at 118° and mixes with water in all proportions. It is a rather weak monobasic acid but forms normal, acid and basic salts. Its reactions are those of its ions. In normal solution it is 0.4 per cent. and in decinormal 1.4 per cent. ionized.

Acetates.—The normal acetates are soluble in water, those of silver and mercurous mercury dissolving with difficulty. Lead, aluminum, iron and copper form sparingly soluble acetates. The alkali acetates combine molecule to molecule with the acid to form acid salts, as $KH(C_2H_3O_2)_2$. The following are the more important reactions of solid acetates:

1. Acetates are decomposed by mineral acids with formation of acetic acid which being volatile may be expelled by heat and recognized by its vinegar-like odor.

2. When strong sulfuric acid and alcohol are added to an acetate and the mixture warmed, ethyl acetate, $C_2H_5C_2H_3O_2$, is formed, a volatile compound with a pleasant odor.

3. When an acetate is heated it blackens and decomposes. The alkali acetates yield a carbonate and acetone, $(CH_3)_2CO$, a volatile compound of peculiar odor. The odor of the decomposition products of these organic compounds cannot be described; it must be learned by experience. Alkali-earth acetates leave the oxid of the metal, and those of the noble metals leave the metal itself.

4. If a dry alkali acetate is heated with arsenous oxid, a very bad smelling, poisonous gas called **cacodyl oxid,** $As_2(CH_3)_4O$, is evolved. This is the **cacodyl reaction** of Bunsen. Other organic acids of the type of acetic acid, such as butyric and valerianic acids, give the same reaction.

Acetate Ion, $C_2H_3O_2^-$.—Solutions of acetic acid and of acetates contain the univalent, colorless acetate ion, $C_2H_3O_2^-$ or CH_3COO^-. Acetic acid is weak being only 0.4 per cent. ionized in normal solution. It is for this reason that the acid is formed when aqueous solutions of acetates, which are rather highly ionized, are treated with the stronger acids. The acetate ions combine with the hydrogen ions to form the undissociated acid,

$$Na^+, C_2H_3O_2^- + H^+, Cl^- \rightleftharpoons HC_2H_3O_2 + Na^+, Cl^-.$$

The effect of a stronger acid is thus weakened by addition of sodium acetate, a large portion of the hydrogen ion being removed from the solution.

Use 0.5 N sodium acetate, $NaC_2H_3O_2, 3H_2O$, equivalent 140.

1. **Sulfuric acid** and **sulfuric acid** with **alcohol** act with acetate ion as they do with dry acetates.

2. **Silver ion** precipitates from rather strong solutions white, crystallin silver acetate, $AgC_2H_3O_2$, soluble in nitric acid and in ammonium hydroxid and in water 10 grams to the liter.

*3. **Ferric ion** (ferric chlorid) colors acetate solutions brown. When the solution is boiled basic ferric acetate precipitates, and when acetate ion is in excess, all the iron is removed. If tartrate ion is present, the reaction does not take place with the iron until the tartrate ion is used up. If iodid ion is present, a reddish brown color may appear because of reduction of ferric to ferrous ion and separation of iodin,

$$2\ Fe^{+++} + 2I^- \rightleftharpoons 2\ Fe^{++} + I_2.$$

In this case the iodin is removed with silver nitrate before adding the ferric solution. In doubtful cases distil the acetate with sulfuric acid and test the distillate. Formic acid acts in a similar way. See under ferric reactions.

OXALIC ACID

Oxalic Acid, $C_2H_2O_4$, $2H_2O$.—Oxalic acid crystallizes in fine colorless, efflorescent, monoclinic needles, soluble in 9 parts of water. It is stronger than acetic acid, the dissociation in decinormal solution being about 15 per cent. Oxalic acid is the simplest diabasic organic acid being composed to two carboxyls, $HOOC^-$ COOH. It forms normal, acid and double salts. The reactions of oxalic acid are those of oxalates and oxalate ion.

Oxalates.—The oxalates of the alkalis and of magnesium are soluble in water, others are generally insoluble, all dissolve in acids. Many insoluble oxalates dissolve in solutions of alkali oxalates forming complex salts.

1. Oxalates are all decomposed by heat with slight carbonization. Those of the alkali and alkali-earth metals yield carbon monoxid and the carbonate or oxid; those of other metals leave the oxid or the metal itself and evolve a mixture of carbon monoxid and carbon dioxid.

2. Sulfuric acid first sets free oxalic acid and then decomposes it into water, carbon dioxid,

$$C_2H_2O_4 = H_2O + CO_2 + CO.$$

If carbonates are present, they should be first decomposed by dilute acid.

Oxalate Ions.—Oxalic acid being dibasic yields two ions, $C_2O_4^{--}$ and $HC_2O_4^{-}$. The neutral salt is usually precipitated.

Use 0.1 N ammonium oxalate, $(NH_4)_2C_2O_4$, H_2O, equivalent 80.

1. **Silver ion** precipitates white, curdy silver oxalate, $Ag_2C_2O_4$, almost insoluble in water, 0.035 gram to the liter, soluble in ammonium hydroxid and in nitric acid.

*2. **Calcium ion** (chlorid) precipitates white calcium oxalate, CaC_2O_4, insoluble in water, (0.0056 gram to the liter), in oxalic acid, and in ammonium oxalate; slightly soluble in acetic acid, easily soluble in strong acids. This is the characteristic reaction and is used for the quantitative determination of calcium.

3. **Barium ion** (chlorid) precipitates white barium oxalate, BaC_2O_4, soluble in acids even acetic and oxalic, and in water 0.112 gram to the liter at 18°.

4. **Lead ion** (acetate) precipitates white lead oxalate, PbC_2O_4, soluble in nitric acid and in water 0.0015 gram to the liter at 18°.

5. **Potassium permanganate** with sulfuric acid oxidizes oxalic acid and oxalates to carbon dioxid and water. Acidify the solution with sulfuric acid, heat to boiling and add the permanganate solution drop by drop. If the solutions are sufficiently concentrated, the escape of the carbon dioxid may be seen and its identity proven by lime-water.

TARTARIC ACID

Tartaric Acid, $C_2H_2(HO)_2(COOH)_2$.—Tartaric acid crystallizes in monoclinic prisms which dissolve in water and in alcohol, but not in ether. Its solution is dextrorotary, that is, turns the plane of polarization to the right. It is a dibasic acid of medium strength, being 13 per cent. ionized in decinormal solution.

Tartaric acid is decomposed by sulfuric acid into water, carbon dioxid, carbon monoxid and carbon.

$$C_2H_6O_6 = H_2O + CO_2 + CO + C_2.$$

Tartrates.—Normal alkali tartrates and acid sodium tartrate are quite soluble in water, the potassium and ammonium acid tartrates are difficultly soluble. Other tartrates dissolve in neutral solutions of alkali tartrates to form double salts, and in tartaric acid to form acid salts.

1 Tartrates are decomposed by mineral acids with liberation of tartaric acid which is decomposed by strong sulfuric acid as indicated above, the carbon residue setting free sulfurous oxid.

2. When heated in a tube tartrates char and evolve vapors which smell like burnt sugar. The residue is carbonate and carbon and effervesces with acids. Ammonium tartrate does not leave carbonate since ammonium carbonate is decomposed by the heat. Metals whose oxids are reduced by carbon are set free. Such are silver, lead, nickel, cobalt, iron and so forth.

Tartrate Ions.—Tartaric acid is dibasic and yields two ions, $HC_2H_4O_6^-$ and $C_2H_4O_5^{--}$. The precipitates are generally normal tartrates.

Use 0.1 N solution of sodium potassium tartrate, Rochelle salt, $NaKC_2H_4O_6$, $4H_2O$, equivalent 147.

1. **Silver nitrate** precipitates from neutral solutions white, curdy silver tartrate, $Ag_2C_2H_4O_6$, soluble in nitric acid and in ammonium hydroxid. When the ammoniacal solution is warmed, silver is deposited as a mirror in the tube. The mirror is best obtained by warming to 70° a mixture which contains just enough ammonium hydroxid to keep the silver tartrate in solution. No free acid must be present. Silver tartrate dissolves in water about 2 grams to the liter.

2. **Potassium ion** in presence of acetic acid precipitates acid potassium tartrate, $KHC_2H_4O_6$, sparingly soluble in water and in acetic acid, easily soluble in mineral acids and in alkali hydroxids and carbonates, soluble in water about 5 grams to the liter.

3. **Lead ion** (acetate) precipitates white, flocculent lead tartrate, $PbC_2H_4O_6$, soluble in nitric acid and in ammonium hydroxid, and in water 0.1 gram to the liter.

4. **Calcium hydroxid** in excess precipitates white calcium tartrate, $CaC_2H_4O_6$, insoluble in acetic acid (difference from oxalates), soluble in water 0.475 gram to the liter.

CITRIC ACID

Citric Acid, $C_3H_4OH(COOH)_3$, H_2O.—Citric acid crystallizes with one molecule of water in rhombic prisms which melt at 100°. It is readily soluble in water and in alcohol. It is tribasic and forms normal, acid and double salts. Its reactions are those of citrates and citrate ions.

Citrates.—Alkali citrates are soluble in water, alkali earth citrates are sparingly soluble, other citrates are insoluble. Insoluble citrates dissolve in solutions of alkali citrates to form complex salts. Calcium citrate dissolves in cold water, but not in hot water. On ignition citrates behave like tartrates. With strong sulfuric acid they carbonize and liberate sulfurous oxid.

Citrate Ions.—Citric acid ionizes in three stages yielding the ions, $H_2C_6H_5O_7^-$, $HC_6H_5O_7^{--}$, $C_6H_5O_7^{---}$. The precipitates are usually normal, and if the third ion does not predominate in solutions, it is produced from the others as fast as it is removed.

Use 0.1 N solution of potassium citrate, $K_3C_6H_5O_7$, H_2O, equivalent 111.

1. **Silver ion** precipitates white silver citrate, $Ag_3C_6H_5O_7$, soluble in nitric acid and in ammonium hydroxid. On warming the ammoniacal solution no silver mirror is formed (difference from tartrate ion), but when the solution is boiled the silver is set free. It dissolves in water at 18° 0.277 gram to the liter.

*2. **Calcium ion** (hydroxid or chlorid) produces no precipitate in cold dilute solution. When the mixture is heated, a white precipitate of calcium citrate, $Ca_3(C_6H_5O_7)_2$, falls, which redissolves on cooling (difference from calcium tartrate). The precipitate is soluble in acetic acid (difference from calcium oxalate) and in water 0.85 gram to the liter at 18°.

3. **Lead acetate** precipitates white amorphous lead citrate, $Pb_3(C_6H_5O_7)_2$, H_2O, soluble in acids, and in water 0.42 gram to the liter at 18°.

Chapter XIII

SEPARATION AND IDENTIFICATION OF THE ACIDS AND ANIONS

The anions do not so generally form insoluble compounds as the kations and the precipitation method of separation is not applicable. Separation is not so necessary, however, since the reactions are generally not interferred with by the presence of the other ions.

A grouping of the anions, based upon their action with a few reagents, is of use to indicate the presence or absence of members of the groups. The reagents used are the ions of barium, lead and silver as found in solutions of barium chlorid, lead acetate and silver nitrate. The application of these reagents, with or without certain acids, and the study of a few characteristic reactions will give information which will in most cases lead easily to the identification of the anions present.

For the group precipitations the solution should be neutral. If it is not so, it must be carefully neutralized with ammonium hydroxid or hydrochloric or nitric acid. The original solution may generally be used, but it may be necessary to replace the kations of the heavy metals by boiling the solution with sodium carbonate. See page 222. Two or three cubic centimeters are used for each test and the operation is conducted in a test-tube or beaker.

GROUPING AND GROUP PRECIPITATION OF THE ANIONS

The anions are grouped and the groups are precipitated as indicated in the scheme which follows:

Group A.—Anions whose barium salts are insoluble in moderately concentrated hydrochloric acid:

Sulfate, SO_4^{--} Fluosilicate, SiF_6^{--}.

To a portion of the solution add dilute hydrochloric acid and barium chlorid. If basic Group 1 is thrown down on adding the acid, filter. A white precipitate indicates the presence of Group

A. If there is a precipitate, filter and use the filtrate for Group B.

Barium sulfate is so finely divided that it is apt to pass through the filter. It filters better when precipitated hot. Use a close filter and pour the liquid through several times. If time permits, let the mixture stand until the precipitate subsides and pour off the clear liquid.

Group B.—Anions whose barium, lead and silver salts are soluble in hydrochloric and nitric acids, but insoluble or slightly soluble in acetic acid:

Fluorid, F^-	Chromate, CrO_4^{--}	Dichromate, $Cr_2O_7^{--}$
Sulfite, SO_3^{--}	Thiosulfate, $S_2O_3^{--}$	Oxalate, $C_2O_4^{--}$.

If Group A was not found, add to a portion of the solution acetic acid and barium chlorid. A white or yellow precipitate proves the presence of Group B. Yellow indicates chromate or dichromate. If Group A was found, filter and add sodium acetate to remove hydrogen ion and to replace hydrochloric with acetic acid. The barium ion present will then precipitate Group B. If the filtrate is very acid, it should be nearly neutralized with ammonium hydroxid before adding the sodium acetate. Thiosulfate ion will be decomposed by the acid in treating for Group A.

Group C.—Anions whose barium, lead and silver salts are slightly soluble in water and readily soluble in acetic acid:

Phosphate, PO_4^{---}	Arsenite, AsO_3^{---}	Arsenate, AsO_4^{---}
Borate, BO_3^{---}	Silicate, SiO_3^{--}	Carbonate, CO_3^{--}
Tartrate, $C_4H_4O_6^{--}$	Citrate, $C_6H_5O_7^{---}$	Hydroxid, HO^-

To a portion of the solution add barium chlorid. A precipitate may include Groups A, B and C. If groups A and B have not been found, it can only be Group C. Pour off the liquid and add acetic acid. If the precipitate wholly dissolves, it is Group C; if none dissolves, Group C is absent. In case of doubt, filter after adding acetic acid and neutralize the filtrate with ammonium hydroxid. The barium ion present will precipitate Group C. Hydroxid ion is precipitated only from the original aqueous so-

lution and when the concentration is above the solubility of $Ba(HO)_2$.

Group D.—Anions whose barium salts are soluble in water and whose silver salts are insoluble or slightly soluble in water and in dilute nitric acid. The group is divided into two sub-groups, the silver salts of the first being insoluble and those of the second soluble in ammonium hydroxid.

1. Insoluble in ammonium hydroxid—

Bromid, Br^- Iodid, I^- Sulfid, S^{--} Ferrocyanid, $Fe(CN)_6^{----}$

2. Soluble in ammonium hydroxid—

Chlorid, Cl^-	**Cyanid, CN^-**	**Thiocyanate, CNS^-**
Iodate, IO_3^-	**Bromate, BrO_3^-**	**Ferricyanid, $Fe(CN)_6^{---}$**
Permanganate, MnO_4^-	**Nitrite, NO_2^-**	

To a portion of the original solution add nitric acid and silver nitrate. A white or colored precipitate proves the presence of Group D. Wash the precipitate and treat it with ammonium hydroxid. If it dissolves, Sub-group 1 is absent. Neutralize the ammoniacal extract with nitric acid. If Sub-group 2 is present, it is reprecipitated.

Silver bromid is somewhat soluble in ammonium hydroxid and, if present in small quantity, may dissolve and pass to Sub-group 2.

Group E.—Anions whose barium, lead and silver salts are readily soluble in water:

Nitrate, NO_3^-	**Cyanate, CNO^-**	**Chlorate, ClO_3^-**
Perchlorate, ClO_4^-	**Formate, CHO_2^-**	**Acetate, $C_2H_3O_2^-$**

If no reagent has yielded a precipitate, only Group E can be present.

Notes.—1. Oxalate, tartrate and citrate ions are not precipitated in the presence of ammonium salts, owing to the formation of soluble double salts.

2. Hypochlorite and hypobromite ions are decomposed by silver nitrate with precipitation of chlorid and bromid of silver.

3. In making the above tests it must be carefully remembered that no substance is absolutely insoluble. The analyst should know approximately the concentration of all the solutions he

uses. He must also note closely the reaction to see when it is complete. Enough of the reagent should be added to complete the precipitation, and no more; enough of the acid is to be used to effect the solution, but no large excess. The excess of acid or alkali is easily recognized by the litmus test. In making this test do not drop the paper in the solution, but apply a drop by means of a glass rod to the paper.

COMPLETE ACIDIC ANALYSIS

The complete acidic analysis may be conducted somewhat as indicated below. In practice the analyst will have to look for only a few anions. The preliminary tests, the basic analysis and the group precipitations will have indicated pretty clearly those which are present. Many anions are decomposed by acids. If they are suggested by the preliminary tests, they must be confirmed by special reactions. It is well for the student to acquire the habit of not relying on one test alone. A conclusion based upon several tests is more satisfactory and at the same time the student thus becomes familiar with a wider field of reactions and properties.

A. **Preliminary Testing.**—If the substance is a solid, it will be well to begin with the preliminary testing with heat and sulfuric acid, as explained in the next chapter. If the substance is a solution or a soluble body, the analysis may proceed at once as below.

B. **Inferences from Basic Analysis.**—A careful consideration of the results of the basic analysis will much simplify the determination of the anions. The more important inferences may be grouped as follows:

1. Arsenic, antimony, tin, chromium and manganese will have been identified, as kations and it will be necessary to examine the original substance to see whether it contained them as anions.

2. If the original substance was soluble in water and dilute hydrochloric acid, no anion could be present which would form with any kation present an insoluble compound. The following exclusions will therefore occur:

a. If basic Group 1 was found, the following anions must be

absent, because their silver and mercurous salts are insoluble in dilute hydrochloric acid:

Cl^-, Br^-, I^-, CN^-, $Fe(CN)_6^{----}$, $Fe(CN)_6^{---}$ (if silver is present), SCN^- (if mercury is present).

b. If basic Group 2 was found, these much be absent:

S^{--}, SO_4^{--} (if lead is present).

c. Basic Group 3 excludes the following:

HO^-, O^{--}, $Fe(CN)_6^{---}$.

d. If the original substance was soluble in water to nearly neutral solution and basic Group 4 was present, the following long list of anions will probably be absent:

HO^-, F^-, S^{--}, CN^-, CNO^-, $Fe(CN)_6^{----}$, $Fe(CN)_6^{---}$, CrO_4^{--}, SiO_4^{--}, CO_3^{--}, $C_2O_4^{--}$, $C_4H_4O_6^{--}$, PO_4^{---}, AsO_4^{---}, AsO_3^{---}, BO_2^-.

e. If basic Group 5 was present, the following are absent with several others if the solution is only slightly acid:

F^-, CO_3^{--}, SO_4^{--}, (except $ZnSO_4$).

f. If only basic group 6 is found, any of the more common anions may be present.

C. **Inferences from Solubilities.**—After the kations have been found an examination of the table of solubilities will give important information with reference to the anions. In a solution no two ions can exist together whose compound is insoluble in the solvent. For example, barium ion cannot remain with sulfate ion in dilute acid solutions, and in neutral solution barium ion precipitates all the anions of Groups A, B and C. So having ascertained what kations are present, a study of the table of solubilities, in connection with a knowledge of the acidity, alkalinity or neutrality of the solution, will show what ions must be absent and what may be present.

D. **Inferences from Mutually Exclusive Anions.**—Oxidizing and reducing anions cannot exist together in a solution, particularly when heated, since they mutually destroy one another. If they are together in the original substance, they will require special treatment. The following two groups are more or less mutually exclusive:

Oxidizers: H_2O_2, NO_2^-, NO_3^-, ClO^-, ClO_3^-, BrO^-, BrO_3^-, $Cr_2O_7^{--}$, MnO_4^-, $Fe(CN)_6^{---}$.

Reducers: H_2O_2, I^-, Br^-, S^{--}, SO_3^{--}, $S_2O_3^{--}$, AsO_3^{---}, NO_2^-, SCN^-, $Fe(CN)_6^{----}$, $C_2O_4^{--}$, $H_4C_4O_6^{--}$.

These anions may be tested for as follows:

For oxidizers: Add to one cubic centimeter of the prepared solution two cubic centimeters of a saturated solution of manganese chlorid in concentrated hydrochloric acid. A dark coloration due to formation of manganic chlorid indicates the presence of an oxidizing agent.

For reducers: Acidify a portion of the prepared solution with sulfuric acid, add a drop of a dilute solution of potassium permanganate and heat to boiling. If the color is not discharged, reducing anions are absent. If the color is bleached only after heating, the reducer is probably oxalate or tartrate ion.

E. **Inferences from Group Precipitation.**—By means of the group precipitations the analyst will be able to reduce the number of anions to be looked for, entire groups being often excluded.

F. **Systematic Examination of the Solution for Anions.**—If the above inferences have been carefully made, there will generally be but little else to do except to confirm the presence of a few anions by special tests. In some cases it may be advisable to make a systematic examination of the substance for all the anions. This may be done according to the scheme here outlined.

For the first of the following operations the original substance or a concentrated aqueous solution is best used. For most of the other operations it will be necessary to use what is known as the **prepared solution,** that is the solution from which the ions of the heavy metals have been removed. See 2, page 222. Each ion found should be confirmed by one or more of the reactions given in the last chapter.

1. Unstable and volatile anions are recognized by the action of the products of their decomposition. Add to a small portion of the original substance or of the concentrated aqueous solution a

little dilute hydrochloric acid and warm gently. If gases are evolved, identify them with proper tests.

a. Milky precipitate of sulphur indicates thiosulfates or polysulfids, or hydrogen sulfid in presence of oxidizers.

b. Separation of iodin indicates iodids in presence of oxidizers.

c. The gases which may be evolved with properties and indications are as follows:

Gas	Properties	Indications	
		Salts	Anions
CO_2	Heavy precipitates lime water	Carbonates	CO_3--
SO_2	Sulfurous odor, bleaches $KMnO_4$	Sulfites	SO_3--
SO_2 & S	Milky precipitate	Thiosulfates	S_2O_3--
N_2O_4	Brown fumes	Nitrites	NO_2-
H_2S	H_2S odor, blackens lead acetate	Soluble sulfids	$S--$ or $HS-$
Cl	Greenish color, chlorin odor	Hypochlorites	$ClO-$ or
		Chlorates	ClO_3-
Br	Brown color, bromin odor	Hypobromites	$BrO-$
HCN	Almond odor, poisonous	Cyanids	$CN-$
O	Accelerates combustion	Peroxids	
$C_2H_4O_2$	Vinegar odor	Acetates	$C_2H_3O_2-$

2. Boil a portion of the original substance or solution with a concentrated solution of sodium carbonate, adding more carbonate, if necessary, until the precipitation is complete. All kations except those of the alkali metals are precipitated as carbonates or hydroxids and are removed by filtration. The filtrate will contain all the anions which were present except those which were decomposed by heat, along with the excess of carbonate ion. This is called the **prepared solution.**

3. Add to a portion of the prepared solution hydrochloric acid in slight excess. A white precipitate of gelatinous H_4SiO_4 indicates silicate ion. Test with metaphosphate bead.

4. Acidify with HCl a portion of the prepared solution and add hydrogen sulfid. Yellow precipitate of As_2S_3 indicates arsenite ion, $AsO_3{}^{---}$, or arsenate ion, $AsO_4{}^{---}$, the latter falling slowly.

5. To another portion of the prepared solution add hydrochloric acid in excess and then barium chlorid. A white pre-

cipitate may be $BaSO_4$ or $BaSiF_6$, indicating sulfate ion, SO_4^{--}, or fluosilicate ion, SiF_6^{--}. Filter, wash and confirm as follows:

a. Sulfate ion.—Mix a portion of the precipitate with sodium carbonate and heat on charcoal with the blow-pipe. Place the mass on a silver coin and moisten with water. A brown or black stain of silver sulfid confirms sulfur.

b. Fluosilicate ion.—Place a portion of the precipitate in a test-tube, dry thoroughly, add a drop or two of sulfuric acid and warm, holding in the mouth of the tube a glass rod moistened with water. White fumes and a cloud of silicic acid in the water on the rod indicates fluosilicate ion. If this is not satisfactory, try the etching test as under fluorid ion.

6. Boil the filtrate from 5, or the prepared solution if sulfate and fluosilicate ions are absent, to remove carbon dioxid, cool, add calcium chlorid and an excess of sodium acetate, filter and wash. A precipitate indicates the possible presence of the following ions:

Fluorid, F^-	Chromate, CrO_4^{--}	Dichromate, $Cr_2O_7^{--}$
Oxalate, C_2O_4	Sulfite, SO_3^{--}	Thiosulfate, $S_2O_3^{--}$

A yellow precipitate indicates dichromate ion, but it might have been chromate in the original substance. Sulfite and thiosulfate ions will probably have been decomposed by the acid and heat and in that case will not be found here. Silicic acid may also occur here.

Confirmations are made as follows:

Fluorid ion.—Treat as under 5 above.

Chromate ion.—The original neutral solution will be yellow and will turn red when made acid.

Dichromate ion.—The original solution will be red and will turn yellow when made alkalin.

Oxalate ion.—The oxalate ion will have been found in the course of the basic analysis. To confirm dissolve a little of the precipitate in warm sulfuric acid, add a very dilute solution of potassium permanganate drop by drop, heating gently. Discharge of the color indicates oxalate ion. No other reducing ion should be present.

Sulfite ion.—This ion will not probably occur here, having been decomposed by the acid in operation 5. It will have been found, however, in the preliminary examination with sulfuric or hydrochloric acid.

Thiosulfate ion.—This ion will have been decomposed by the acid and heat and will not occur here. It will have been found in the preliminary examination.

7. Add to the filtrate from 6 barium hydroxid to alkalin reaction. A precipitate indicates the possible presence of the following:

Phosphate, PO_4---	Arsenite, AsO_3---	Arsenate, AsO_4---
Borate, BO_2-	Silicate, SiO_4----	Carbonate, CO_3--
Tartrate, $C_4H_4O_6$--	Citrate, $C_6H_5O_7$---	Hydroxid, HO-

Confirmation may be made as follows:

Phosphate ion.—Phosphate ion will have been found in the basic analysis. For further confirmation add to the prepared solution nitric acid and ammonium molybdate. A yellow precipitate of ammonium phosphomolybdate indicates phosphate ion.

Arsenite and arsenate ions.—Arsenic will have been found in the basic analysis and its form in the original substance will be recognized by the tests given under arsenic in the last chapter.

Borate ion.—Moisten a little of the precipitate of 7 in a dish or watch-glass, add alcohol and ignite. A green flame indicates borate ion. (See under Boron.)

Silicate ion.—Test the precipitate of 7 or the original substance with a metaphosphate bead; or dry and heat with calcium fluorid and sulfuric acid and expose to the fumes a drop of water in a loop of platinum wire. A cloud of silicic acid in the water indicates silicate ion.

Carbonate ion.—Carbonate ion will have been found in the treatment of the original substance with acids.

Tartrate ion.—If carbonization takes place when the solution is evaporated to dryness and the residue ignited, or when the original substance is heated, tartrates may be present, otherwise they are absent. Heated with sulfuric acid they give the odor of burnt sugar.

The silver test for tartrate ion may be made as follows: To the aqueous or hydrochloric acid solution of the original substance add potassium carbonate to alkalin reaction, evaporate till crystals begin to form, add acetic acid in slight excess, then alcohol to precipitation. Let stand a few minutes, filter, wash with a little ether and dry. Remove the precipitate to a test-tube, dissolve in a little water, add silver nitrate solution and enough of ammonium hydroxid to just dissolve the precipitate. Warm gently for a few minutes by placing the tube in a beaker of boiling water. The coating of the tube with a silver mirror proves the presence of the tartrate ion.

Citrate ion.—Silver nitrate precipitates white silver citrate, $Ag_3C_6H_5O_7$, soluble in ammonium hydroxid, but the ammoniacal solution does not form the silver mirror when warmed.

Calcium chlorid gives no precipitate in the cold, but on heating the mixture white calcium citrate, $Ca_3(C_6H_5O_7)_2$, falls (difference from oxalic acid).

Hydroxid ion.—This ion must be sought for in the original aqueous solution.

8. Acidify a portion of the prepared solution (solution of 2) with nitric acid and add silver nitrate. Shake well and wash the precipitate by decantation. A precipitate indicates the possible presence of the following:

1. Bromid, Br^-	Iodid, I^-	Sulfid, S^{--}	Ferrocyanid, $Fe(CN)_6^{---}$
2. Chlorid, Cl^-	Cyanid, CN^-	Iodate, IO^-	Thiocyanate, CNS^-
Bromate, BrO_3^-	Nitrite, NO_2^-	Permanganate, MnO_4^-	Ferricyanid, $Fe(CN)_6^{---}$.

If the solution is very dilute, nitrite may not be precipitated. If it is concentrated, acetate and formate from the next group may be thrown down. Hypochlorite and hypobromite are decomposed by silver nitrate with precipitation of silver chlorid, bromid, bromate and chlorate (if sufficiently concentrated, more than 10 per cent.). They will also have been decomposed by heat in the preparation of the solution. They need only be looked for here when the original solution is used.

Add ammonium hydroxid to the precipitate and shake well.

If the precipitate dissolves at once, Sub-group 1 is absent; if it dissolves slowly or incompletely, some of the ions of this Sub-group are present.

Confirmations are made as follows:

Sulfid ion.—If any of basic Group 2 was found, sulfid ion is absent. The preliminary treatment with acids will have revealed its presence. If further confirmation is desired, test as follows: (*a*) Warm the original or prepared solution with nitric acid, or (*b*) Add zinc acetate, filter, wash and warm the precipitate with dilute hydrochloric acid. Evolution of hydrogen sulfid proves sulfid ion present.

Iodid ion.—If iodid ion is present, the group precipitate will be yellow. Acidify a portion of the prepared solution with sulfuric or nitric acid, add a little potassium nitrite and a few drops of chloroform and shake. A violet color indicates iodid ion.

Bromid ion.—If bromid ion is present the group precipitate will have a pale color. If iodin is absent, acidify with sulfuric or nitric acid, add a few drops of chloroform, then chlorin water drop by drop, shaking well. A yellow color indicates bromid ion.

If iodin is present along with bromin, acidify, add potassium nitrite, boil until the iodin is expelled, then add chloroform and chlorin water.

Chlorid ion.—The white curdy precipitate of silver chlorid is generally satisfactory evidence. Confirm by formation of chromyl chlorid as follows: Evaporate a portion of the prepared solution to dryness, mix with an equal quantity of potassium dichromate and cover with sulfuric acid. Red fumes of chromyl chlorid, CrO_2Cl_2, indicate chlorid ion. Conduct the fumes into a drop of very dilute sulfuric acid. A transient blue color due to perchromic acid is further confirmation.

If bromin and iodin are present, they may be oxidized and removed by means of potassium permanganate as follows (Jannash and Kuester): To a portion of the prepared solution add an equal volume of acetic acid and heat to boiling. Add permanganate solution acidified with sulfuric acid drop by drop

with continued boiling until the color persists. Filter from the precipitated manganese dioxid, if necessary, add a few drops of alcohol to remove the excess of permanganate, boil off the excess of alcohol and add silver nitrate. The precipitate of white silver chlorid, insoluble in nitric acid and soluble in ammonium hydroxid confirms chlorin.

Cyanid and thiocyanate ions are also removed by the above process.

With a little practice, chlorin, bromin and iodin together in a solution may be identified by fractional precipitation. Acidify the solution with nitric acid, warm and add drop by drop with vigorous shaking decinormal solution of silver nitrate. Note the color produced by each drop and allow the precipitate to settle before adding the next drop. Yellow silver iodid first falls, then pale yellow silver bromid and finally white silver chlorid. The main difficulty is to tell when the bromid begins to precipitate. It is well to filter when the iodin seems to have been all removed, then add sufficient silver nitrate to precipitate the bromid and chlorid together, filter, wash two or three times by decantation, then add a strip of zinc and some dilute sulfuric acid. Bromid ion is formed and the solution may be tested with chlorin for bromin in the usual way.

Ferrocyanid ion.—Acidify the prepared solution with hydrochloric acid and add ferric chlorid. A blue precipitate of ferric ferrocyanid, $Fe_4(FeC_6N_6)_3$, indicates ferrocyanid ion. If the color is masked by the presence of thiocyanid ion, it will be brought out by addition of mercuric chlorid.

Ferricyanid ion.—Acidify with hydrochloric acid and add ferrous sulfate. Blue ferrous ferricyanid, $Fe_3(FeC_6N_6)_2$, indicates ferricyanid ion.

Thiocyanate ion.—Acidify with hydrochloric acid and add ferric chlorid. A red color, in the absence of nitrite or iodid, indicates thiocyanate ion. If the result is doubtful, acidify with sulfuric acid, add stannous chlorid and boil, collecting the gas in a trap or tube containing ferric chlorid.

Cyanid ion.—To a portion of the prepared solution add a

very little sodium hydroxid and a few drops of ferrous sulfate solution and heat to boiling. Add a drop of ferric chlorid and acidulate with hydrochloric acid. A precipitate or blue coloration of ferric ferrocyanid indicates cyanid ion.

In the presence of ferrocyanid, ferricyanid or thiocyanate ion, neutralize with hydrochloric acid, and solid sodium hydrogen carbonate and distill. The cyanid ion pases over and the distillate is treated as directed in last paragraph.

Iodate ion.—Iodate ion will not usually be found in the presence of iodid ion or of reducing agents. If iodids are not present, add ferrous sulfate and starch. The ferrous ion reduces the iodate, setting free the iodin which colors the starch blue. If much iodin is liberated, the starch is not necessary. Sulfurous oxid may also be used as the reducer.

If iodid and iodate are both present, acidulate with acetic acid. The iodid reduces the iodate and the solution becomes brown from the separation of iodin.

Bromate ion.—(*a*) Acidify the prepared solution slightly with sulfuric acid and add manganous sulfate. A red coloration followed by a black precipitate of manganese dioxid on boiling indicates bromate ion. This test holds in the presence of iodates and chlorates, which give no change of color, and no precipitate.

(*b*) If a brown color appears on addition of sulfuric acid, bromate or iodate ion in presence of bromid ion is indicated.

Permanganate ion.—If permanganate ion is present, the solution will have the familiar reddish color of this ion. Acidify with sulfurous acid and add sodium sulfite. Discharge of color indicates permanganate ion. The colorless solution may be tested for manganous ion.

Nitrite ion.—Apply any of the tests for nitrite ion to the prepared solution or to the aqueous extract of the original substance. See under nitrous acid.

Hypochlorite ion.—The hypochlorite ion is decomposed when acid is added to the solution and should be found in the preliminary examination. If its presence is suspected use for confirmation an aqueous extract of the original substance, make it

alkalin with sodium carbonate and add acetic acid drop by drop, shaking well. Add a bit of litmus paper; bleaching and chlorous odor indicates hypochlorite ion. Permanganate ion must be absent, as it would also oxidize the litmus.

Hypobromite ion.—Hypobromite ion acts very much like hypochlorite ion. It will be generally recognized by the peculiar bromous odor emitted when solutions containing it are acidified.

9. If neither barium chlorid nor silver nitrate has given a precipitate, all of the anions which have been considered may be regarded as absent unless they have been found in the preliminary testing.

The following , however, may have been present:

Nitrite, NO_2-	Nitrate, NO_3-	Hypochlorite, $ClO-$
Hypobromite, $BrO-$	Cyanate, $CNO-$	Chlorate, ClO_3-
Perchlorate, ClO_4-	Formate, CHO_2-	Acetate, $C_2H_3O_2-$

Hydrogen peroxid, H_2O_2 Sodium peroxid, Na_2O_2

If the test for oxidizers with manganous chlorid gave no color, the following must be absent:

Nitrite, NO_2-	Nitrate, NO_3-	Hypochlorite, $ClO-$
Hypobromite, $BrO-$	Chlorate, ClO_3-	Perchlorate, ClO_4-

Hydrogen peroxid, H_2O_2 Sodium peroxid, Na_2O_2

If there was color, all must be looked for. Nitrate ion produces the color only in concentrated solution.

Nitrite ion.—See page 228.

Nitrate ion.—Make a concentrated aqueous extract of the original substance, add ferrous sulfate solution or a crystal of the salt and pour down the side of the tube concentrated sulfuric acid so that it underlies the solution. A brown zone at the line of separation of the liquids indicates nitrate ion (in the absence of nitrite ion). See under nitrate ion, Chapter XII.

If nitrite ion is present, it must be removed, a process somewhat difficult because of the ease with which it is oxidized to nitrate ion. Neutralize with ammonium hydroxid, add ammonium chlorid and boil until a portion of the solution does not at once give a blue color with potassium-iodid-starch solution, then proceed as in last paragraph.

Hypochlorite ion.—See page 228. For further confirmation add to a portion of the solution a drop of mercury and shake. A yellow coating of mercuric oxid on the surface of the mercury indicates hypochlorite ion.

Hypobromite ion.—See page 229.

Cyanate ion.—*a.* Neutralize a portion of the prepared solution with dilute hydrochloric acid, concentrate by evaporation and add a strong solution of cobalt acetate. A blue color due to alkali cobaltocyanate, $Na_2CoC_4N_4O_4$, indicates cyanate ion. If the color does not appear add a little alcohol. Thiocyanates act in the same way and cyanids interfere with the reaction.

b. Add to a portion of the prepared solution sodium hydroxid and boil until ammonia, if present, is all expelled, cool and acidify with sulfuric acid. Evolution of CO_2 indicates cyanate or carbonate ion. Boil to expel CO_2 (and H_2S if present) and make alkalin with NaHO. Evolution of ammonia gas indicates cyanate ion. See under cyanate ion in the last chapter.

Chlorate ion.—Chlorate ion will have been found in the preliminary testing with sulfuric acid. Further confirmation may be made as follows

a. Add to the prepared solution nitric acid to acidify, then silver nitrate to remove acidic Group D, shake well, filter and add to the filtrate sodium sulfite in excess to reduce the chlorate to chlorid ion. A white precipitate of silver chlorid indicates chlorate ion.

b. If hypochlorite ion was found, it must be removed because of its tendency to form chlorid and chlorate ions. Add nitric acid in very slight excess, potassium iodid just enough to decompose the hypochlorite ion, potassium nitrite to remove the excess of KI, then boil off the free iodin. Now apply the test as directed in *a.*

Perchlorate ion.—Remove chlorid and chlorate ions if they are present as in test under chlorate ions. The filtrate from the silver chlorid precipitate will contain the perchlorate ion with the excess of silver ions. Boil, cool, add sodium hydroxid to excess to precipitate the silver, evaporate to dryness, ignite to

convert the perchlorate into chlorid, extract with hot nitric acid and add a drop of silver nitrate. A residue or precipitate of silver chlorid indicates perchloric acid.

Formate ion.—Formate ion will have been detected in the preliminary examination with sulfuric acid by means of its familiar odor. To confirm add to the prepared solution mercuric chlorid and warm. A white precipitate of mercurous chlorid indicates formate ion.

Acetate ion.—Acetate ion will have been recognized by its vinegar odor in the preliminary testing. To confirm make the solution exactly neutral and add ferric chlorid. A red coloration with a red precipitate on boiling indicates acetate ion.

The formate ion gives a similar reaction, but the odors and the mercuric chlorid test will suffice to distinguish between it and the acetate ion. Acetate ion also reduces mercuric chlorid, but not so readily as formate ion.

Hydrogen peroxid.—(*a*) Acidify a portion of the original solution with sulfuric acid and add a drop of potassium dichromate solution. A blue color indicates hydrogen peroxid.

(*b*). Add to another portion of the solution a solution obtained by mixing a drop of ferric chlorid and a drop of potassium ferrocyanid with a little water. A blue or green color of Prussian blue indicates hydrogen peroxid.

Sodium peroxid.—The same as for hydrogen peroxid.

PART IV

Chapter XIV

COMPLETE ANALYSIS OF AN UNKNOWN

For the complete systematic analysis of an unknown substance the procedure may take place in steps as follows:

1. Preliminary examination.
2. Bringing the substance into solution.
3. Basic analysis.
4. Acidic analysis.
5. Conclusion as to the composition and nature of the unknown.

The scheme presented in this book includes the more common elements and the principal inorganic compounds and a few of the more important compounds of carbon.

1. PRELIMINARY EXAMINATION

A. The substance is a gas.

Gases are readily identified by their color, odor, combustibility, solubility and a few other properties. The odor of some gases is characteristic and is sufficient itself for their identification. The odors cannot be described and should be learned practically. The student should become familiar with the characteristic properties of the gases so as to recognize them whenever they are evolved in the preliminary testing or in the course of the analysis.

Colored gases:—

Chlorin.—Greenish color, chlorous odor, incombustible, bleaches litmus, sets iodin free.

Chlorin tetroxid, Cl_2O_4.—Greenish color, chlorous odor, bleaches litmus, explodes when heated.

Bromin.—Reddish brown color, bromous odor, incombustible, bleaches faintly, oxidizes, displaces iodin.

Iodin.—Violet color, iodous odor, incombustible, sublimes condensing to steel-gray solid.

Nitrogen tetroxid, N_2O_4.—Reddish yellow color, nitrous odor, soluble in water, darkens ferrous sulfate solution.

Nitrogen trioxid, N_2O_3.—Same as nitrogen tetroxid.

Chromyl chlorid, CrO_2Cl_2.—Dark red color, peculiar odor, condenses to blood-red liquid, decomposed by water.

Colorless gases:—

Hydrogen.—Very light, odorless, burns with pale blue flame forming water, explosive when mixed with air or chlorin.

Oxygen.—Odorless, incombustible, supports combustion, inflames glowing splinter, makes explosive mixture with hydrogen, darkens solution of pyrogallic acid.

Nitrogen.—Odorless, insoluble, incombustible, does not support combustion, very inactive.

Nitrogen dioxid, N_2O_2.—Insoluble, turns brown in contact with air, accelerates combustion, unites to oxygen to form soluble N_2O_3 or N_2O_4.

Ammonia, NH_3.—Characteristic ammonia odor, incombustible, turns litmus blue, very soluble in water to alkalin solution.

Cyanogen, C_2N_2.—Odor of bitter almonds, burns with peach-blossom flame, soluble in water, white precipitate with silver nitrate, *very poisonous*.

Carbon monoxid, CO.—Slightly pungent odor, insoluble in water, burns with pale blue flame to CO_2.

Carbon dioxid, CO_2.—Scarcely odorous, heavier than air, slightly soluble in water, incombustible, does not support combustion, makes cloud in lime-water.

Hydrocarbon compounds.—Burn with yellow flame, making CO_2 and H_2O.

Hydrogen sulfid, H_2S.—Hydrogen sulfid odor, blackens lead acetate paper, precipitates metallic sulfids, burns with pale blue flame and sulfurous odor.

Sulfurous oxid, SO_2.—Sulfurous odor, acid taste, incombustible, soluble in water, reducing agent, decolorizes permanganate solution.

B. The substance is a liquid.

Water.—Colorless, odorless, tasteless, incombustible, no residue on evaporation, boils at 100°, freezes at 0°. If it is a native water, there will be a residue on evaporation of the dissolved solids.

Carbon disulfid, CS_2.—Carbon disulfid odor, insoluble, volatile, dissolves sulfur and phosphorous, burns with pale blue flame and sulfurous odor.

Alcohol, C_2H_6O.—Alcoholic odor, burning taste, miscible with water, dissolves iodin to brown solution, burns with faintly luminous flame to CO_2 and H_2O.

Ether, $C_4H_{10}O$.—Ethereal odor, not miscible with water, very volatile, burns with luminous flame to CO_2 and H_2O.

Benzene, C_6H_6.—Benzene odor, not miscible with water, very volatile, burns with smoky flame.

Liquid hydrocarbons.—Petroleum odor, not miscible with water, burn with yellow, smoky flame. Include gasoline, benzine, kerosene and so forth.

Mercury.—This is the only liquid metal. It is recognized by its high specific gravity, 13.595, and its metallic luster.

Solutions.—Solutions leave a residue on evaporation except in the case of dissolved substances which are volatile or decomposable, such as gases, some acids, volatile liquids, and a few salts. In any case, proceed with basic and acidic analysis.

C. The substance is a solid.

1. Examine the substance as to physical properties, color, odor, taste, luster, crystallin form, specific gravity, hardness, and draw such conclusions as seem to be justified. For example, if the solid is colorless, it can hardly contain chromium; if it is colored, it cannot be any of the common colorless salts.

2. Examine the substance as to its solubility. If it dissolves readily in water or dilute hydrochloric acid, the analyst may proceed at once with basic and acidic analysis. If it is found insoluble, the preliminary testing should be continued. Even if it is soluble, much information may be gained by the further examination of the solid.

3. Observe the action of water upon the substance. Chemical action takes place between water and many substances with characteristic phenomena. The water may be decomposed, or the substance may undergo change, or hydrolysis may take place in various ways. In the following table are given the more important actions which are to be looked for. The evolved gases are recognized by properties which have been given elsewhere.

a. Evolution of a gas.—

Hydrogen.—Alkali or alkali-earth metals.

Oxygen.—Peroxids, especially those of hydrogen or sodium.

Ammonia.—Alkali-earth nitrids.

Phosphin.—Alkali and alkali-earth phosphids; has phosphorous odor and burns with yellow flame.

Hydrogen sulfid.—Sulfids of aluminum and magnesium. Sulfids of the alkalis and the alkali-earth metals may undergo a sufficient decomposition to yield the odor of hydrogen sulfid.

Haloid acids.—Halids of certain negative elements, especially phosphorous.

Acetylene.—Carbids of certain metals, especially calcium, has acetylene odor and burns with white, smoky flame.

b. Change of form.—

By hydrolysis.—Crystallin salts of bismuth and antimony become amorphous oxysalts.

By hydration.—Amorphous anhydrous salts become hydrous and crystallin and generally change color; salts of copper, cobalt and so forth.

4. Observe the action of sulfuric acid on the substance. This action will give important information, particularly with reference to the anions. The original solid or the strong solution should be treated with the acid first dilute then concentrated. Heat may be applied, though generally the heat of the reaction will be sufficient.

a. Dilute sulfuric acid.

Dilute sulfuric acid will produce effects similar to those brought about by dilute hydrochloric acid and these have already been

discussed under the systematic examination of the solution for anions in the last chapter.

b. Concentrated sulfuric acid.

The concentrated acid liberates the same gases as the dilute acid, but its action is more powerful, and many compounds are decomposed which do not yield to the latter. Those gases which are given in the former list are not repeated here unless they come from a different source. The acid should be added drop by drop to a small portion of the substance, since the action is sometimes violent.

Colorless gases	Properties	Indications
O	Accelerates combustion	Peroxids, chromates, permanganates
CO	Burns with blue flame	Oxalates, tartrates, cyanids
CO_2	Clouds lime water	Oxalates
HCl	Fumes, precipitates Ag Cl	Chlorids
HF	Fumes, etches glass	Fluorids, fluosilicates
H_2S	H_2S odor, blackens lead acetate	Sulfids
SO_2	Sulfurous odor, bleaches $KMnO_4$	Sulfites, thiosulfates
Cl	Greenish yellow, chlorin odor	Chlorids with oxidizers
Cl_2O_4	Yellow, explosive, chlorin odor	Chlorates
Br&H Br	Brown, turns starch yellow	Bromids
I & HI	Violet	Iodids
NO_2&N_2O_3	Brown, nitrous odor	Nitrates, nitrites
CrO_2Cl_2	Blood-red, peculiar odor	Chlorids with chromates

5. Heat a small portion in a test-tube, holding the tube inclined.

a. Water is expelled and condenses on the tube. This indicates salts containing water of crystallization, or hydrous substances which give up the water when heated, or organic matters which yield water on decomposition. It must be remembered that there is always a small amount of adherent moisture which is expelled by the heat.

b. A sublimate forms on the tube, which is easily moved by heat from place to place.

1. The sublimate is white.

Ammonium salts.—Odor of ammonia when heated with alkali hydroxids.

Arsenous oxid, As_2O_3.—Heated with charcoal gives metallic arsenic.

Antimonous oxid, Sb_2O_3.—Reduced with charcoal without metallic luster.

Mercury salts.—Heated with Na_2CO_3 gives red HgO.

2. The sublimate is yellow.

Arsenous sulfid, As_2S_3.—Reacts for arsenic as above.

Mercury salts.—React as above. The iodid changes color to red when touched with a glass rod.

Sulfids.—Sulfur condenses in red drops in the tube.

3. The sublimate is gray or black.

Mercury compounds.—Finely divided mercury.

Arsenic compounds.—Arsenic sublimate in presence of reducers.

Iodids.—Iodin in presence of oxidizers, violet vapor.

c. The color changes.

Organic matters carbonize when heated, becoming gray or black. When strongly ignited in contact with the air, they burn up.

Some metallic oxids change color when heated and assume the original color when cooled.

d. Gases are evolved, resulting from decomposition. These are recognized and identified as under A.

Oxygen.—From unstable oxids, nitrates, chlorates and so forth.

Sulfurous oxid.—From sulfur, sulfids and from sulfates in presence of reducing agents.

Sulfuric oxid.—From sulfates of heavy metals and from sulfuric or disulfuric acid. Heavy white stifling fumes.

Nitrogen tetroxid.—From nitrates.

Carbon dioxid.—From carbonates and oxalates.

Bromin.—From bromids in presence of oxidizers.

Iodin.—From iodids.

Cyanogen.—From cyanids.

Ammonia.—From ammonium salts or from cyanids.
Chlorin.—From chlorids in presence of oxidizers.
Hydrogen sulfid.—From sulfur compounds in presence of water or organic matters.
Odor of garlic.—From compounds of arsenic.
Empyreumatic odor.—From organic compounds.

6. Reduce with sodium carbonate on charcoal.

The substance in powder is mixed with twice its weight of sodium carbonate, placed in a little depression in the coal and heated in the blow-pipe reducing flame. Most metallic compounds may thus be reduced. Some oxids and easily reduced carbonates yield to the coal alone.

a. Metallic bead without sublimate.
Gold.—Yellow, malleable, insoluble in nitric acid.
Silver.—White, malleable, soluble in nitric acid.
Tin.—White, easily fusible, converted by nitric acid into white metastannic acid, H_2SnO_3.
Copper.—Red mass, hard to fuse, soluble in nitric acid.
Iron, cobalt, nickel.—Gray masses, magnetic, soluble in CHl.
Platinum.—Gray mass, infusible, malleable, insoluble in acids.

b. Metallic bead with sublimate.
Antimony.—White, brittle; white sublimate.
Bismuth.—White, brittle; brown sublimate.
Lead.—White or lead color, malleable, soft; yellow sublimate.

c. Sublimate without bead.
Arsenic.—White, arsenous oxid, odor of garlic.
Cadmium.—Brown, cadmium oxid.
Zinc.—Zinc oxid, white when cold, yellow when hot.

d. Fusion without reduction to metal.
Manganese.—Fusion green, turning red when moistened in air.
Chromium.—Green infusible mass, yellow in presence of oxidizers.
Sulfur.—Colored mass which blackens moistened silver.

e. White unfused mass: magnesium, aluminum, barium, strontium, calcium. Moisten with cobalt nitrate and heat.

Magnesium.—Flesh color.

Aluminum.—Blue.

Barium, strontium, calcium.—Gray.

7. Bead reactions.

The colors which metallic oxids impart to beads of borax and salt of phosphorous on platinum wire are characteristic and often serve for the identification of metals. A bead of the reagent is made in a loop of the wire by dipping the hot wire in the salt and holding it in the Bunsen flame, repeating the operation until the loop is filled and the bead transparent. By moistening the bead and touching it to the powdered substance a small portion is taken up. This is heated first in the oxidizing flame and then in the reducing flame. The colors obtained have the significance indicated in the table below.

a. Metaborate bead.

Color of bead	Oxidizing flame	Reducing flame
Gray		Ag, Pb, Bi, Sb, Cd, Zn, Ni
Yellow	Fe, Ag, Ni	
Brown	Ni	
Green	Cr, Cu (hot)	Cr, Fe
Blue	Co, Cu, (Cold)	Co
Red	Fe, Ni	Cu
Violet	Ti, Ni (with Co)	Mn
Colorless	SiO_2	SiO_2, Mn, Cu

b. Metaphosphate bead.

The metaphosphate bead gives almost the same colors as the borax bead. Silicic oxid and silicates give no color, but in the metaphosphate bead the silica is less soluble and forms a floating cloud within the bead called the *silica skeleton.*

8. Flame colorations.

A small portion of the powdered substance is brought into the Bunsen flame on a platinum wire. It is generally best to moisten the substance with hydrochloric acid. The colors may be masked by the presence of other metals and, except in the

case of sodium or potassium, is only reliable when but one metal is present. The principal flame colors are as follows:

Sodium.—Yellow, monochromatic light. Sealing wax and potassium dichromate appear yellow when illuminated by sodium light.

Potassium.—Violet color, which is completely masked if sodium is present. If the flame is viewed through blue cobalt glass, the yellow light is intercepted and the potassium flame appears pink.

Lithium.—Carmine red flame, which may be confounded with the strontium flame.

Strontium.—Carmin red, very much like the lithium flame

Calcium.—Brick-red, not very brilliant.

Barium, boron, manganese.—Greenish yellow flame.

Thallium.—Emerald-green.

Copper.—Generally green flame, sometimes blue (cuprous chlorid).

Lead, arsenic, antimony.—Light blue flame not very characteristic.

9. Spectrum.

The spectroscope serves to identify several of the metals, even in the presence of others. The instrument should have a refracting prism at the slit so that two sources of light may be observed at once. The identification is made quite sure if the spectrum of the unknown is brought in juxtaposition with that of the known substance. If the instrument is furnished with a scale, let the divisions of the scale be noted where the spectrum lines of the unknown appear, and then compare with the actual spectrum of the metal supposed to be present.

The more important spectra are shown in the spectrum chart and may be described as follows:

Sodium.—Bright, double yellow line.

Lithium.—A bright red line.

Thallium.—A bright line in the green.

Potassium.—A faint line in the red and a fainter one in the violet.

Calcium.—A band in the red and one in the yellow.
Barium.—Bands in the red, yellow and green.
Strontium.—Several lines in the orange and a bright line in the blue.

2. BRINGING THE SUBSTANCE INTO SOLUTION

It is necessary to have the substance in solution before beginning the basic and acidic analysis. The solution should be systematically made and much information may be gained by carefully observing the action of the substance with the various solvents.

1. Treat a small portion of the substance with water, first cold, then hot. If there is no residue, the unknown contains no compound insoluble in water. In this case dissolve a sufficient quantity and proceed with the basic and acidic analysis. Do not fail at this point to study the table of solubilities. All compounds insoluble in water may at once be excluded.

Most substances are more or less soluble in water. For practical purposes those which dissolve less than one part in one hundred may be regarded as insoluble.

2. If the substance does not all dissolve, filter and evaporate a few drops of the filtrate on platinum foil. If there is a residue, the unknown is a mixture of soluble and insoluble compounds. Treat the undissolved portion again in order to be sure that the residue is not due to an insufficient quantity of water.

3. Treat the portion which was not dissolved by water with hydrochloric acid, first dilute, then concentrated, using heat if necessary. If there is complete solution, nothing can be present which is insoluble in water and hydrochloric acid. In this case basic Group 1 will be absent. This solution may be mixed with the aqueous solution unless a precipitate is formed on bringing them together. In this case they must be examined, separately.

4. If there is still an undissolved portion, examine it first to see if it consists of the chlorids of basic Group 1. If it does not, treat it with nitric acid cold and hot. Substances soluble in nitric acid are generally soluble in hydrochloric acid and vice versa.

The compounds insoluble or difficulty soluble in the acids are AgCl, AgBr, AgI, AgCN, AuCl, $PtCl_2$, $BaSO_4$, $SrSO_4$, $PbSO_4$, HgS, CaF_2, SnS_2, SiO_2, fused $PbCrO_4$, the strongly ignited oxids Al_2O_3, Cr_2O_3, SnO_2, Sb_2O_3, ferrocyanids except those of the alkali and alkali-earth metals, many silicates, carbon and sulfur.

5. The residue not soluble in hyrdochloric acid or nitric acid is treated with aqua regia. Of the salts insoluble in the single acids the following pass into solution: $PtCl_2$, AuCl, HgS, Sb_2O_3, SnS_2, ferrocyanids and ferricyanids. AgBr, AgI and AgCN are more or less converted into AgCl.

The following remain undissolved: AgCl, AgBr, AgI, AgCN, $BaSO_4$, $SrSO_4$, $PbSO_4$, fused $PbCrO_4$, CaF_2, Al_2O_3, Cr_2O_3, native Sb_2O_3, SnO_2, sulfur, carbon, many silicates, some other rare elements and compounds.

6. In order to bring these insoluble substances into solution it is necessary to subject them to special treatment as described below. We should first know, however, what is present. This knowledge will have been gained in most cases by the preliminary examination. If further information seems desirable, it may be obtained as follows:

a. Silver, lead and tin.—Reduce a small portion of the undissolved residue on charcoal before the blow-pipe.

No metallic button is obtained; silver, lead and tin are absent.

A metallic button is obtained; silver, lead or tin may be present.

Flatten the button and treat with nitric acid. If there is a white residue of metastannic acid, tin is present; if the solution is clear, tin is absent.

Add to a portion of the solution hydrochloric acid. If there is a white, curdy precipitate of silver chlorid, silver is present.

Add to a portion of the solution sulfuric acid. If there is a white precipitate of lead sulfate, lead is present.

b. Sulfates of lead, strontium and barium.—Boil a portion of the undissolved residue with concentrated solution of sodium carbonate. Lead and strontium sulfates are transformed into carbonates, while the barium sulfate remains almost unchanged.

Pour off the liquid or filter and add an excess of concentrated hydrochloric acid. If all dissolves barium is absent; if a portion remains, it is barium sulfate, possibly some strontium sulfate that escaped the action of the carbonate. Filter and wash.

Test the filtrate for lead, strontium, barium and sulfate ions.

The undissolved barium sulfate may be fused with alkali carbonates or reduced on charcoal and tested for sulfur by the hepar reaction.

c. Sulfur and carbon.—These elements will have been recognized in the preliminary testing. They may be removed by ignition of the residue.

d. Lead chromate. Heat on a platinum foil with sodium carbonate and potassium nitrate. Dissolve in a little water. If the mass is yellow chromium is indicated. To a portion of the solution add silver nitrate; chocolate silver chromate indicates chromium. To the other portion add sulfuric acid; white lead sulfate indicates lead.

e. The other insoluble compounds may be looked for as in the preliminary testing, but they will be found any way in the analysis of the product of the fusion of the insoluble residue in alkali carbonates.

7. Special treatment of insoluble substances.

1. Silver halids.—Add to a portion of the residue insoluble in the acids a bit of zinc and some dilute sulfuric acid and let the action continue for a few minutes. The nascent hydrogen reduces the silver halid. Pour off the liquid and test it for the halogen and cyanogen. Treat the residue with nitric acid and add to the solution chlorid ion. A precipitate of silver chlorid indicates the presence of silver.

2. Lead sulfate.—Boil a portion of the undissolved residue with sodium carbonate, then with water; or boil with a solution of ammonium acetate. Treat the solution for lead and sulfate ions.

If lead and silver are present, free or combined, they must be removed before proceeding. The process may be continued in their presence by using a porcelain or iron crucible for the

fusion of the next paragraph. In this case, however, aluminum, silicon and iron may be introduced. Carbon and sulfur should also be removed by ignition.

3. Fuse the balance of the residue insoluble in acids with four times its weight of fusion mixture as directed in 2 under "Testing for Silicates" in Chapter XII. Do not forget that platinum cannot be used if lead or silver compounds are present. These metals make a fusible alloy with platinum and the crucible will be destroyed.

The solution is examined for acids which can be present.

The residue is dissolved in hydrochloric acid and must be examined for the metals which can be present.

3. BASIC ANALYSIS

1. If the original substance is soluble in water or in dilute hydrochloric acid, the solution needs no preparation for basic analysis. Proceed as directed in Part 2.

2. If the substance is totally dissolved in dilute hydrochloric acid, or in concentrated acid with subsequent dilution, no preparation of the solution is necessary, and Group 1 of the kations is absent, since hydrochloric acid is the precipitant for this group. The residue left on treatment of the substance with hydrochloric acid may be only the chlorids of Group 1.

3. If nitric acid is used for dissolving the substance, remove the excess of acid by evaporating to dryness, dissolve the residue in water, add hydrochloric acid and proceed to test for the ions of Group 2.

4. If there is a residue insoluble in acids, it will often be best to analyze this separately from the acid solution.

4. ACIDIC ANALYSIS

Make the inferences from basic analysis, make preliminary tests, prepare the solution, and carry out the analysis as directed in Part 3.

5. CONCLUSIONS AS TO THE NATURE AND COMPOSITION OF THE UNKNOWN

1. The analysis will show what elements and, to a large extent, what radicals were present in the unknown.

2. If free elements are present, they are identified by their properties.

3. The preliminary testing will, in many cases, indicate the compounds which are present.

4. If only one metal and one acid radical has been found, the substance was evidently the salt of this metal and acid.

5. If two kations and two anions have been found, two, three or four salts may have been present. A study of the preliminary experiments, the way the mixture acts with the reagents, and the physical properties of the original substance, will often enable one to arrive at pretty safe conclusion as to the compounds present.

6. If several anions and several kations are present, it will be possible to tell only approximately what compounds were in the original sample. If the substance was in fragments, these may be examined separately and their properties carefully compared with the properties of the compounds which can be present.

PART V

REAGENTS AND TABLES

Chapter XV

REAGENTS

Reagents should be strictly chemically pure and the solutions should be carefully prepared to the required strength. Weighing to the nearest gram or half gram will be sufficient. The alkalis and the salts which make alkalin solutions by hydrolysis attack the glass of the bottle and in the course of time cause flakes of silica to appear. These should be filtered off; or better, the solutions should be prepared often in small quantities.

In preparing solutions dissolve the required amount of the substance in distilled water, transfer to a graduated liter flask, rinse the vessel a few times with water, add the washings to the solution, then fill the flask to the mark with distilled water. Mix thoroughly and transfer to the bottle in which the solution is to be kept Half or quarter liter quantities may be prepared in the same way.

Reagent bottles should generally have ground glass stoppers, but those which are to contain alkalis are better closed with rubber. Compounds sensitive to light are kept in colored bottles. Such are hydrogen sulfid, ammonium sulfid, silver nitrate and potassium permanganate.

SOLVENTS

Water, H_2O. Distilled. The general solvent for qualitative solutions is water. Other liquids are used only in special cases. The water should be distilled to free it from dissolved solids. The dissolved gases do not, as a rule, interfere with qualitative reactions. The gas-free water is prepared when needed. Rain water, carefully collected and kept, answers quite well for gen-

eral qualitative use. It should be tested, however, from time to time to ascertain what substance it may contain in traces.

Alcohol, C_2H_6O.—Commercial 95 per cent. alcohol.

Alcohol absolute.—Free from water as possible.

Carbon disulfid.—CS_2.—Commercial carbon disulfid.

Ether, $(C_2H_5)_2O$.—Commercial ether.

Ether-alcohol.—A mixture of equal volumes of ether and absolute alcohol.

GASES

Hydrogen, H_2.—Prepared by action of zinc on dilute sulfuric acid. Used as a reducing agent and usually evolved in the vessel containing the substance upon which it is to act.

Hydrogen sulfid, H_2S.—Prepared in special apparatus by action of ferrous sulfid upon dilute sulfuric or hydrochloric acid of specific gravity 1.1. Generally used as gas and conducted into the solution through a glass tube. The saturated solution is also used and its strength is about 0.15 N.

Sulfurous Oxid, SO_2.—Prepared by the action of hot concentrated sulfuric acid upon copper. It is used as a reducing agent, either as gas or in solution. The solution, sulfurous acid, is prepared by conducting the gas through water to saturation. The solution should be freshly prepared since it slowly oxidizes to sulfuric acid.

Oxygen.—Prepared by heating a mixture of two parts potassium chlorate and one part manganese dioxid. May be kept in a gas holder for use when needed.

Carbon dioxid, CO_2.—Prepared by the action of hydrochloric acid on lime-stone or marble. May be generated when needed.

ACIDS

Dilute acids of half the strength indicated will serve most purposes equally well.

Acetic acid, $C_2H_4O_2$.—Equivalent 60, glacial acid 17 N, sp. gr. 1.055.

Dilute: Solution 5 N, sp. gr. 1.04, 30 per cent. $C_2H_4O_2$. Dilute 300 grams or 285 cc. of glacial acid to one liter.

Chlorplatinic acid, H_2PtCl_6.—The solution contains 5 per cent. of platinum. Dissolve 5 grams of platinum in aqua regia, evaporate to dryness, add a little hydrochloric acid, evaporate nearly to dryness, and add water to 100 cc. A solution one-tenth as strong will answer many purposes equally well.

Hydrochloric acid, HCl.—Equivalent 36.45, sp. gr. 1.2, 11 N, 40.8 per cent. HCl.

Dilute: 5 N, sp. gr. 1.09, 18.3 per cent. HCl. Dilute 372 cc. of the concentrated acid to one liter. Take specific gravity and add enough acid to bring it up to 1.09.

Very dilute: Normal, sp. gr. 1.0045, 3.6 per cent. HCl. Dilute 200 cc. of the 5 N acid to one liter.

Nitric acid, HNO_3.—Equivalent 63, 16 N, sp. gr. 1.42, 65 per cent. HNO_3.

Dilute: 5 N, sp. gr. 1.2, 30 per cent. HNO_3. Dilute 345 cc. of the concentrated acid to one liter. Take the specific gravity and add acid to bring it up to 1.2.

Very dilute: Normal, sp. gr. 1.04, 6.3 per cent. HNO_3. Dilute 200 cc. of the 5 N acid to one liter.

Nitrohydrochloric acid (aqua regia).—Mix 3 volumes of hydrochloric acid with one volume of nitric acid. The concentrated or the dilute acids are used according to the strength desired. The usual strength is 5 N. Prepare as needed.

Phosphoric acid, H_3PO_4.—Equivalent 32.67, 26 N, sp. gr. 1.7, 85 per cent. H_3PO_4.

Dilute: 5 N, sp. gr. 1.15, 16.3 per cent. H_3PO_4. Dissolve 192 grams of 85 per cent. acid in water and make up to one liter.

Very dilute: Normal, sp. gr. 1.016, 3.26 per cent. H_3PO_4. Dilute 200 cc. of the 5 N acid to one liter.

Sulfuric acid, H_2SO_4.—Equivalent 49, 36 N, sp. gr. 1.84, 96 per cent. H_2SO_4. The container should be kept carefully closed, as the acid absorbs moisture from the air and dilutes.

Dilute: 5 N, sp. gr. 1.18, 24.5 per cent. H_2SO_4. Dilute 110 cc. of the concentrated acid to one liter, take specific gravity and add enough acid to bring it up to 1.18. Because of its attraction for moisture the concentrated acid will generally be a little be-

low its standard strength. This is the proper strength for generating hydrogen.

Dilute: 2 N, sp. gr. 1.07, 10 per cent. H_2SO_4. Dilute 400 cc. of the 5 N acid to one liter. This is the proper strength for the generation of hydrogen sulfid.

Very dilute: Normal, sp. gr. 1.03, 4.9 per cent. H_2SO_4. Dilute 200 cc. of the 5 N acid to one liter.

Sulfurous acid, H_2SO_3.—The solution saturated at 15° contains about 16.5 per cent. of H_2SO_3. On exposure to air it gradually weakens from loss of SO_2. It is unstable, the sulfurous acid gradually oxidizing to sulfuric acid. The sulfurous oxid gas is generally used instead of the solution

Tartaric acid, $C_4H_6O_6$.—Equivalent 75, normal, sp. gr. 1.34, 7.5 per cent. $C_4H_6O_6$. Dissolve 75 grams in water and make up to one liter. The acid is unstable in solution and should be freshly prepared when needed.

BASES

Ammonium hydroxid, NH_4HO.—Equivalent 35, concentrated solution 17 N, sp. gr. 0.09 contains 60 per cent. NH_4HO. Container should be kept carefully closed, as the solution loses strength by escape of ammonia.

Dilute: 5 N, sp. gr. 0.965, 17.5 per cent. NH_4HO. Dilute 333 cc. of concentrated ammonium hydroxid to one liter.

Very dilute: Normal, sp. gr. 0.992, contains 3.5 per cent. NH_4HO. Dilute 200 cc. of the dilute solution to one liter.

Barium hydroxid, BaH_2O_2.—Equivalent 85.7, saturated solution about 0.33 N. Mix an excess of the solid with water and let stand for twenty-four hours, shaking occasionally. Let settle until clear and decant into small bottles.

Calcium hydroxid, CaH_2O_2.—Equivalent 37, saturated solution about 0.05 N. Add an excess of quick lime to water, let stand for twenty-four hours, with frequent shaking, and siphon off the clear solution.

Potassium Hydroxid. KHO.—Equivalent 56, solution 5 N, sp. gr. 1.26, contains 28 per cent. KHO. Dissolve 312 grams in

water and make up to one liter. The stick potassium hydroxid usually contains about 90 per cent. KHO.

One-half the above strength for most purposes.

Dilute: Normal, sp. gr. 1.045, contains 5.6 per cent. KHO. Dilute 200 cc. of the 5 N solution to one liter.

Sodium hydroxid, NaHO.—Equivalent 40, solution 5 N, sp. gr. 1.24, contains 20 per cent. NaHO. Dissolve 220 grams in water and bring up to one liter. Stick sodium hydroxid contains usually about 90 per cent. NaHO.

One-half the above strength for most purposes.

Dilute: Normal, sp. gr. 1.046, contains 4 per cent. NaHO. Dilute 200 cc. of the 5 N solution to one liter.

Bottles containing alkalis should be closed with rubber stoppers, since the glass sticks badly. The solutions should be exposed to the air as little as possible, since they absorb carbon dioxid, becoming carbonate.

SALTS

Ammonium carbonate, $(NH_4)_2CO_3$.—Equivalent 48, solution 5 N, sp. gr. 1.081, contains 24 per cent. $(NH_4)_2CO_3$. Dissolve 200 grams of the crystallized salt, which has the formula NH_4HCO_3, $NH_4CO_2NH_2$, in 200 cc. 5 N ammonium hydroxid and dilute with water to one liter.

Ammonium chlorid, NH_4Cl.—Equivalent 53.45, solution 5 N, sp. gr. 1.07, contains 26.7 per cent. NH_4Cl. Dissolve 267 grams of ammonium chlorid in water and make up to one liter.

Ammonium molybdate, $(NH_4)_2MoO_4$.—Equivalent 98, for MoO_3 72, solution normal. Dissolve 72 grams of molybdic oxid in 400 cc. of normal ammonium hydroxid and pour with stirring into 600 cc. of 5 N nitric acid. Let it stand and siphon off from any precipitate which may form. Keep in green glass.

Ammonium oxalate, $(NH_4)_2C_2O_4$, $2H_2O$.—Equivalent 80, solution 0.5 N, contains 3.1 per cent. $(NH_4)_2C_2O_4$. Dissolve 40 grams of the crystallized acid in water and make up to one liter.

Ammonium sulfid, $(NH_4)_2S$.—Equivalent 34, solution about 4 N. Saturate 500 cc. of 5 N ammonium hydroxid with hydrogen sulfid, forming NH_4SH, then add 5 N ammonium hydroxid to

one liter. This solution should be colorless. It decomposes slowly and should be prepared at short intervals.

Ammonium sulfid, yellow, $(NH_4)_2S_x$.—Add a little powdered roll sulfur to 4 N ammonium sulfid solution. Avoid excess of sulfur as it produces red polysulfids. The solution should be yellow and not red.

Barium chlorid, $BaCl_2,2H_2O$.—Equivalent 122, solution 0.5 N, sp. gr. 1.1. Dissolve 61 grams in water and make up to one liter.

Calcium chlorid, $CaCl_2,6H_2O$.—Equivalent 109.5, solution 0.5 N, sp. gr. 1.04. Dissolve 55 grams in water and make up to one liter.

Calcium nitrate, $Ca(NO_3)_2,4H_2O$.—Equivalent 118, solution 0.1 N, sp. gr. 1.03. Dissolve 59 grams in water and make up to one liter.

Calcium sulfate $CaSO_4,2H_2O$.—Equivalent 86, saturated solution about 0.03 N.

Copper sulfate, $CuSO_4,5H_2O$.—Equivalent 124.8, solution 0.5 N, sp. gr. 1.04. Dissolve 62.4 grams in water and make up to one liter.

Cobalt nitrate, $Co(NO_3)_2,6H_2O$.—Equivalent 145.5 solution 0.5 N, contains 72.7 grams to the liter.

Ferric chlorid, $FeCl_3,6H_2O$.—Equivalent 90.1, solution 3 N, contains 270 grams to the liter. Add a few drops of HCl to prevent hydrolysis.

Ferrous sulfate, $FeSO_4$, $7H_2O$.—Equivalent 139, solution 0.5 N, sp. gr. 1.03. Dissolve 69.5 grams in water, make up to one liter and add a few drops of sulfuric acid. The solution easily oxidizes to ferric sulfate and should be prepared at short intervals. Solution of ferrous ammonium sulfate may be used.

Lead acetate, $Pb(C_2H_3O_2)_2,3H_2O$.—Equivalent 189.6, solution 0.5 N, contains 94.8 grams to the liter. A few drops of acetic acid should be added to prevent formation of lead carbonate.

Magnesia mixture.—Solution normal. Dissolve 101.5 grams of $MgCl_26H_2O$ and 107 grams of NH_4Cl in water, add 300 cc. 5 N ammonium hydroxid and make up to one liter.

Magnesium sulfate, $MgSO_4,7H_2O$.—Equivalent 123.2, solution 0.5 N, contains 61.6 grams to the liter.

Mercuric chlorid, $HgCl_2$.—Equivalent 135.4, solution 0.2 N. Dissolve 27 grams in water and make up to one liter.

Mercurous nitrate, $Hg_2(NO_3)_2,2H_2O$.—Equivalent 280, solution 0.2 N. Dissolve 56 grams in 50 cc. 5 N nitric acid, and dilute to one liter. Add a drop of mercury.

Potassium chromate, K_2CrO_4.—Equivalent 97.3, solution 0.5 N, contains 48.6 grams to the liter.

Potassium cyanid, KCN.—Equivalent 65.2, solution one-half normal, contains 32.6 grams to the liter. The solution does not keep well and should be prepared fresh from time to time.

Potassium dichromate, $K_2Cr_2O_7$.—Equivalent 49, one-sixth the molecular weight for oxidation, solution normal, 49 grams to the liter.

Potassium ferricyanid, $K_3Fe(CN)_6$.—Equivalent 109.8, solution one-half normal, contains 54.9 grams to the liter.

Potassium ferrocyanid, $K_3Fe(CN)_6, 3H_2O$.—Equivalent 105.7, solution one-half normal, contains 52.8 grams to the liter.

Potassium iodate, KIO_3.—Equivalent 36, one-sixth the molecular weight for oxidation, solution 0.5 N, 18 grams to the liter.

Potassium iodid, KI.—Equivalent 166, solution one-fifth normal, contains 33 grams to the liter.

Potassium iodomercurate, K_2HgI_4.—Nessler's solution. See page 254.

Potassium permanganate, $KMnO_4$.—Equivalent 31.6, one-fifth the molecular weight for oxidation, solution normal, 31.6 grams to the liter.

Potassium sulfate, K_2SO_4.—Equivalent 87, solution 0.5 N, contains 43.5 grams to the liter.

Potassium thiocyanate, KCNS.—Equivalent 97, solution 0.5 N, 48.6 grams to the liter.

Silver nitrate, $AgNO_3$.—Equivalent 170, solution 0.05 N, contains 8.5 grams to the liter.

Sodium acetate, $NaC_2H_3O_2,3H_2O$.—Equivalent 136, solution 0.5 N, contains 68 grams to the liter.

Sodium carbonate, Na_2CO_3.—Equivalent 53, solution normal, sp. gr. 1.05. Dissolve 53 grams of the dry salt in water and make up to one liter. The crystallin salt has 10 molecules of water. If this is used take 143 grams.

A 3 N solution should be prepared by dissolving 159 grams of the dry salt or 429 grams of crystals in one liter of water.

Sodium cobaltinitrite, $Na_3Co(NO_2)_6$.—Equivalent 134, solution 0.1 N, contains 13.4 grams to the liter.

Sodium phosphate, $Na_2HPO_4,12H_2O$.—Equivalent 119, solution 0.5 N, 59.5 grams to the liter.

Sodium sulfite, $Na_2SO_3,7H_2O$.—Equivalent 126, solution 2 N, contains 252 grams to the liter.

Sodium sulfid, Na_2S.—Equivalent 39, solution 5 N. Saturate 5 N sodium hydroxid with hydrogen sulfid.

Sodium thiosulfate, $Na_2S_2O_3,5H_2O$.—Equivalent 124, solution 0.5 normal, contains 62 grams to the liter.

Stannous chlorid, $SnCl_2,2H_2O$.—Equivalent 113, solution 0.5 N. Dissolve 56.4 grams in 100 cc. of concentrated hydrochloric acid, dilute to one liter and add a few pieces of tin; or better, dissolve 30 grams of tin foil in concentrated HCl and make up to one liter.

Stannous chlorid, strong solution for Bettendorff test for arsenous acid. Dissolve 60 grams of granulated tin in 100 cc. of concentrated HCl, heating if necessary. If the metal does not all dissolve, pour off the liquid and add to it a few drops of HCl and a few bits of tin.

Uranyl acetate, $UO_2(C_2H_3O_2)_2,H_2O$.—Equivalent 203, solution 0.1 N, contains 20.3 grams to the liter.

DRY REAGENTS

Ammonium carbonate, $(NH_4)_2CO_3$. See page 250.

Borax. See sodium tetraborate.

Calcium fluorid, CaF_2.

Calcium oxid, CaO.

Copper.

Ferrous sulfate. $FeSO_4,7H_2O$.

Fusion mixture, equimolecular parts of dry sodium and potassium carbonates, with or without potassium nitrate.

Iron, nails and filings.

Lead dioxid, PbO_2.

Lime, calcium oxid or hydroxid.

Manganese dioxid, MnO_2.

Microcosmic salt, $NaNH_4HPO_4,H_2O$.

Potassium carbonate, K_2CO_3.

Potassium chlorate, $KClO_3$.

Potassium cyanid, KCN.

Potassium nitrate, KNO_3.

Potassium nitrite, KNO_2.

Potassium hydrogen sulfate, $KHSO_4$.

Sodium, metal.

Sodium carbonate, Na_2CO_3.

Sodium tetraborate, $Na_2B_4O_7,10H_2O$.

Zinc, dust and metal.

SPECIAL REAGENTS

Bromin water.—Saturated solution, 0.46 N, contains 3.66 per cent. bromin. Should be kept in dark, glass-stoppered bottles.

Brucin.—Dissolve 1 gram in 100 cc. strong sulfuric acid.

Chlorin water.—Saturated solution, about 0.2 N, contains 0.73 per cent. of chlorin. Should be prepared often and kept in dark colored bottles.

Iodin water.—Dissolve 50 grams of potassium iodid in one liter of water and add an excess of iodin, shaking from time to time. Decant from the undissolved iodin. The solution is approximately 0.25 N.

Indigo solution.—Add in small portions 4 grams of finely powdered indigo to 10 cc. disulfuric acid, mix thoroughly and let stand 48 hours. Pour with stirring into 80 cc. of water and filter.

Nessler's reagent.—Dissolve 35 grams potassium iodid and 13 grams mecuric chlorid in 800 cc. water and add saturated solution of mercuric chlorid until the red precipitate just persists. Add 160 grams potassium hydroxid and make up to 1000 cc. To

make the solution sensitive add to the portion about to be used a little more mercuric chlorid.

Phenylenediamin (meta), $C_6H_4(NH_2)_2$.—Dissolve 2 grams in 10 cc. strong hydrochloric acid and make up to 100 cc. with water. Decolorize with bone black if necessary.

Potassioscope liquid.—Dissolve 0.5 gram gentian blue in a liter of alcohol. Place in flat bottles such that the layer of liquid is about an inch thick.

Starch-iodid mixture.—Add one gram of pulverized starch to 10 cc. of water and boil for a few minutes, then add one gram of potassium iodid. Shake well each time before using.

Sulfanilic acid mixture.—Dissolve 0.5 gram of sulfanilic acid in 150 cc. of 5 N acetic acid. Boil 0.1 gram of alpha naphthylamin with 25 cc. water, let it settle and decant the clear solution into 50 cc. of 5 N acetic acid. Mix the two solutions thus obtained. The mixture should be nearly colorles. If it is not, shake it with a little zinc dust or bone black and filter.

INDICATORS

Litmus paper.—This may be bought, or it may be prepared by dipping paper in litmus solution.

Litmus solution.—Digest 10 grams of powdered litmus in boiling water, pour off the liquid and treat the residue again once or twice with boiling water. The extract thus obtained is allowed to settle. The clear blue liquid is decanted or filtered and made up to 200 cc. The solution is usually slightly alkalin, as indicated by the deep blue color, while neutral litmus is violet. Very dilute nitric acid is added, by dipping a glass rod in the acid and stirring the solution with it, until the neutral violet color appears. The bottle should be kept loosely corked, as the color fades unless exposed to the air.

Methyl orange.—Dissolve one gram in one liter of water.

Phenolphthalein.—Dissolve one gram in 100 cc. alcohol.

Turmeric paper.—Turmeric paper can be bought from dealers, or it may be prepared by steeping paper in turmeric solution.

TABLES

Table of International Atomic Weights

The atomic weights given in the following table are computed from the atomic weight of oxygen taken as 16. They are those adopted by the International Committee on Atomic Weights, which is appointed jointly, from time to time, by the American, English, German, and French Chemical Societies.

	Symbol	O = 16		Symbol	O = 16
Aluminum	Al	27.1	Molybdenum	Mo	96.0
Antimony	Sb	120.2	Neodymium	Nd	144.3
Argon	A	39.88	Neon	Ne	20.2
Arsenic	As	74.96	Nickel	Ni	58.68
Barium	Ba	137.37	Niton		222.4
Bismuth	Bi	208.0	Nitrogen	N	14.01
Boron	B	11.0	Osmium	Os	190.9
Bromin	Br	79.92	Oxygen	O	16.00
Cadmium	Cd	112.40	Palladium	Pd	106.7
Cæsium	Cs	132.81	Phosphorus	P	31.04
Calcium	Ca	40.07	Platinum	Pt	195.2
Carbon	C	12.00	Potassium	K	39.10
Cerium	Ce	140.25	Praseodymium	Pr	140.6
Chlorin	Cl	35.46	Radium	Ra	226.4
Chromium	Cr	52.0	Rhodium	Rh	102.9
Cobalt	Co	58.97	Rubidium	Rb	85.45
Columbium	Cb	93.5	Ruthenium	Ru	101.7
Copper	Cu	63.57	Samarium	Sa	150.4
Dysprosium	Dy	162.5	Scandium	Sc	44.1
Erbium	E	167.7	Selenium	Se	79.2
Europium	Eu	152.0	Silicon	Si	28.3
Fluorin	F	19.0	Silver	Ag	107.88
Gadolinium	Gd	157.3	Sodium	Na	23.00
Gallium	Ga	69.9	Strontium	Sr	87.63
Germanium	Ge	72.5	Sulfur	S	32.07
Glucinum	Gl	9.1	Tantalum	Ta	181.5
Gold	Au	197.2	Tellurium	Te	127.5
Helium	He	3.99	Terbium	Tb	159.2
Hydrogen	H	1.008	Thallium	Tl	204.0
Indium	In	114.8	Thorium	Th	232.4
Iodin	I	126.92	Thulium	Tu	168.5
Iridium	Ir	193.1	Tin	Sn	119.0
Iron	Fe	55.84	Titanium	Ti	48.1
Krypton	Kr	82.9	Tungsten	W	184.0
Lanthanum	La	139.0	Uranium	U	238.5
Lead	Pb	207.10	Vanadium	V	51.0
Lithium	Li	6.94	Xenon	X	130.2
Lutecium	Lu	174.0	Ytterbium	Yt	172.0
Magnesium	Mg	24.32	Yttrium	Y	89.0
Manganese	Mn	54.93	Zinc	Zn	65.37
Mercury	Hg	200.6	Zirconium	Zr	90.6

Maximum Equivalent Ionic Conductivities at 18°
After Kohlrausch and others

Kations	Conductance	Temp. coef.	Anions	Conductance	Temp. coef.
H^+	318.00	....	HO^-	174.00	0.0238
Li^+	33.44	0.0265	F^-	46.64	0.0238
Na^+	43.55	0.0244	Cl^-	62.0	0.0216
K^+	64.67	0.0217	Br^-	67.63	0.0215
Rb^+	67.6	0.0214	I^-	66.4	0.0213
Cs^+	68.2	0.0212	NO_3^-	59.0	0.0205
NH_4^+	64.4	0.0222	ClO_3^-	55.03	0.0215
Tl^+	66,0	0.0215	BrO_3^-	46.28	.....
Ag^+	54.02	0.0229	IO_3^-	33.88	0.0234
$\frac{1}{2}Mg^+$	46.0	0.0256	ClO_4^-	64.7	.....
$\frac{1}{2}Ca^+$	53.0	....	MnO_4^-	53.4	.....
$\frac{1}{2}Sr^+$	54.0	....	SCN^-	56.63	0.0211
$\frac{1}{2}Ba^+$	56.3	0.0238	CHO_2^-	46.7	.....
$\frac{1}{2}Cd^+$	47.4	....	$C_2H_3O_2^-$	35.0	.....
$\frac{1}{2}Zn^+$	46.6	0.0251	$\frac{1}{2}SO_4^-$	68.7	0.0227
$\frac{1}{2}Pb^+$	61.5	0.2043	$\frac{1}{2}CO_3^-$	70.0	0.0270

Ionization of Acids, Bases and Salts

In the following table is given the percentage of ionization of various compounds at 18° calculated from electric conductivities. The concentration is indicated by the character within the parenthesis.

Acids	Per cents.	Bases	Per cent.	Salts	Per cents.
HNO_3 (Conc.)	9.6	NaHO (N)	73.0	K_2SO_4 (N)	53.0
HNO_3 (N)	82.0	NaHO (0.1 N)	91.0	K_2SO_4 (0.1 N)	56.0
HNO_3 (0.1 N)	94.0	KHO (N)	77.0	KNO_3 (N)	64.0
HCl (Conc.)	13.6	KHO (0.1 N)	91.5	$KClO_3$ (N)	79.0
HCl (0.1 N)	94.0	LiHO (N)	63.0	$AgNO_3$ (N)	58.0
H_2SO_4 (Conc.)	0.7	LiHO (0.1 N)	90.0	$CaSO_4$ (0.1 N)	63.0
H_2SO_4 (N)	51.0	NH_4HO (N)	0.4	$BaCl_2$ (N)	58.0
H_2SO_4 (0.1 N)	62.0	NH_4HO (0.1 N)	1.5	$CaCl_2$ (N)	58.0
H_2SO_3 (0.1 N)	8.0	$Ca(HO)_2$ (N)	70.0	Na_3PO_4 (N)	45.0
HBr (0.5 N)	90.0	$Ca(HO)_2$ ($\frac{1}{64}$ N)	90.0	Na_2CO_3 (N)	40.0
HI (N)	7.0	$Ba(HO)_2$ (N)	69.0	Na_2SO_4 (N)	44.5
HI (0.5 N)	90.0	$Ba(HO)_2$ ($\frac{1}{64}$ N)	92.0	$ZnCl_2$ (N)	48.0
H_3PO_4 (0.5 N)	17.0	$Sr(HO)_2$ ($\frac{1}{64}$ N)	93.0	$ZnSO_4$ (N)	24.0
$C_2H_4O_2$ (N)	0.4			$CuSO_4$ (N)	22.0
$C_2H_4O_2$ (0.1 N)	1.3	Salts		$FeSO_4$ (N)	24.0
$C_2H_2O_4$ (0.1 N)	15.0	NaCl (N)	68.0	$KC_2H_3O_2$ (N)	64.0
$C_2H_6O_6$ (0.1 N)	13.0	NaCl (0.1 N)	84.0	$NaC_2H_3O_2$ (N)	53.0
H_2CO_3 (0.1 N)	0.17	KCl (N)	75.0	$Pb(C_2H_3O_2)_2$ (N)	34.0
H_2S (0.1 N)	0.07	KBr (N)	76 0	$HgCl_2$ (N)	0.01
H_3BO_3 (0.1 N)	0.013	KI (N)	78.0	$Hg(CN)_2$ (N)	very low
HCN (0.1 N)	0.01	NH_4Cl (N)	74.0		

Table of Aqueous Solubilities.

The numbers indicate grams to the liter of the aqueous solution generally at 18°. They have been taken from the works of Comey, Seidel, Weigel, Landolt-Boernstein and others. A few of the numbers are uncertain because of hydrolysis or other decomposition. Only those solubilities which are under 10 grams to the liter have been included.

Antimony		Ferrous		Silver	
sulfid	0.001	carbonate	0.07	acetate	10.0
Arsenous		hydroxid	0.07	borate	9.0
sulfid	0.0005	sulfid	0.006	bromate	1.5
Barium		Lead		bromid	0.00008
arsenate	0.55	bromid	8.3	carbonate	0.017
bromate	6.5	carbonate	0.00006	chlorid	0.0015
carbonate	0.022	chlorid	10.0	chromate	0.025
chromate	0.0038	chromate	0.0002	citrate	0.28
citrate	0.04	citrate	0.42	cyanid	0.0002
ferrocyanid.	1.0	fluorid	0.64	dichromate	0.083
fluorid	1.6	hydroxid	0.017	hydroxid	0.02
fluosilicate	0.26	iodate	0.019	iodate	0.04
iodate	0.22	iodid	0.6	iodid	0.000002
molybdate	0.058	oxalate	0.0018	oxalate	0.037
oxalate	0.09	oxid.	0.017	oxid	0.021
tartrate	0.25	phosphate	0.00013	phosphate	0.064
thiosulfate	0.5	sulfate.	0.42	sulfate.	8.0
sulfate	0.0025	sulfid.	0.0009	sulfid.	0.0145
sulfite	0.01	tartrate	0.1	tartrate	2.0
Bismuth		thiocyanate	4.5	thiocyanate	0.00014
sulfid	0.00018	thiosulfate	0.3	Sodium	
Bismuthyl		Magnesium		diantimonate	2.5
chromate	0.0008	carbonate	0.97	Stannic	
Cadmium		fluorid	0.076	sulfid.	0.0002
hydroxid	0.0026	fluosilicate	0.4	Stannous	
oxalate	0.033	hydroxid	0.009	sulfid.	0.00002
sulfid	0.0013	oxalate	0.3	Strontium	
Calcium		Manganese		carbonate	0.01
carbonate	0.013	hydroxid	0.0055	chromate	1.2
citrate	0.084	sulfid	0.0063	fluorid.	0.12
fluorid	0.015	Mercuric		hydroxid	7.0
bicarbonate.	0.385	bromid	6.0	iodate	0.26
hydroxid	1.16	hydroxid	0.05	molybdate	0.1
iodate	2.5	iodid	0.05	oxalate	0.05
oxalate	0.006	oxid.	0.05	oxid.	0.7
oxid	1.2	sulfid.	0.0244	sulfate.	0.11
silicate	0.095	Mercurous		sulfite	0.033
sulfate.	2.0	bromid	0.00004	tartrate	1.7
sulfite	1.2	chlorid	0.00047	Zinc	
tartrate	0.185	iodid	0.0000002	carbonate	0.01
Cobalt		sulfate.	0.6	cyanid	4.0
iodate	8.3	Nickel		hydroxid	0.0013
sulfid	0.0038	hydroxid		iodate	8.7
Copper		sulfid.	0.0036	oxalate	0.0064
sulfid	0.0181	Potassium		sulfid	0.0068
tartrate	0.42	fluosilicate.	1.25	tartrate	0.22

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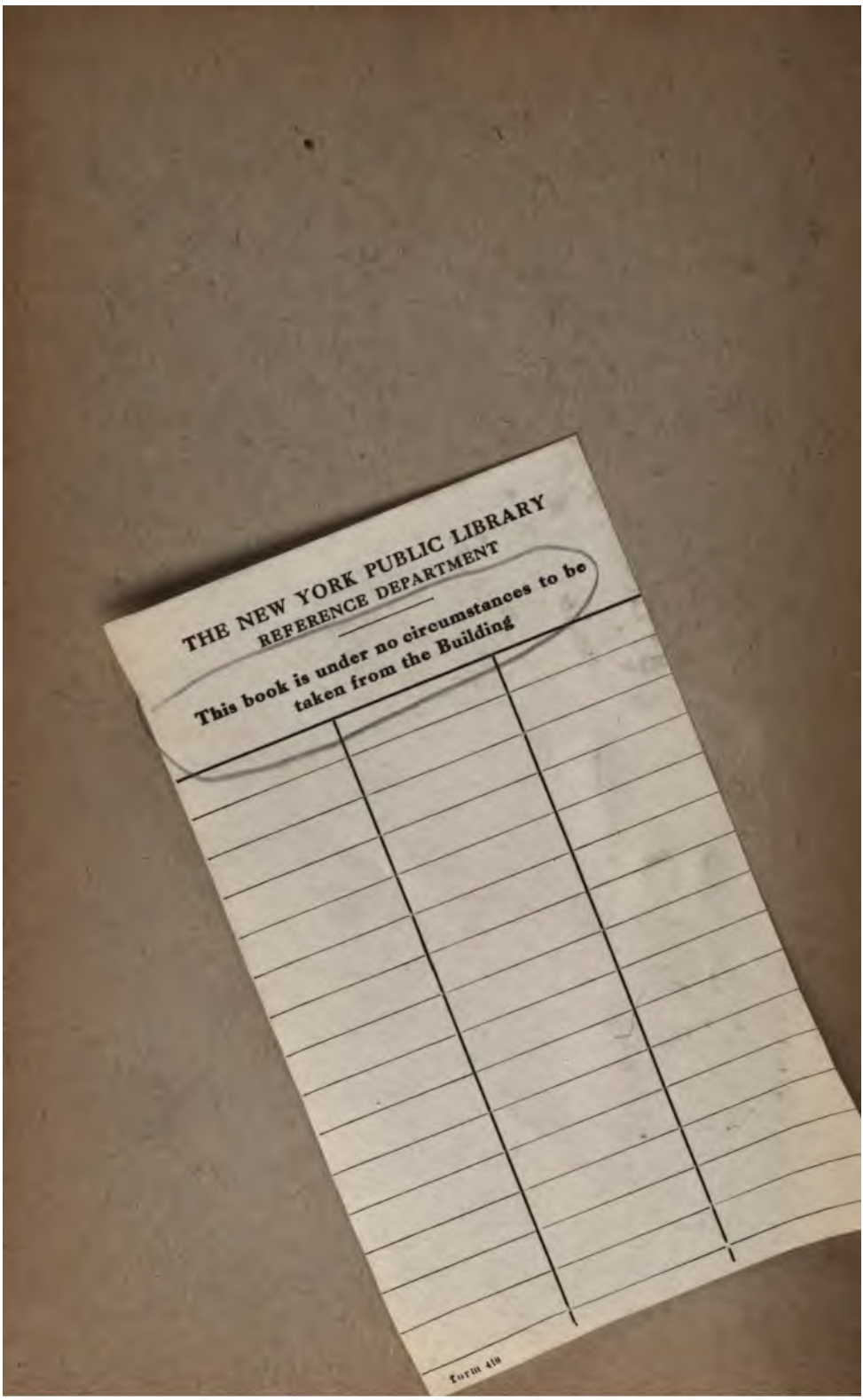
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